PB80-203623

Evaluation of Ammonia 'Fixation' Components in Actual Refinery Sour Waters

American Petroleum Inst.
Washington, DC

Prepared for

Robert S Kerr Environmental Research Lab.
Ada, OK

May 80

U.S. Department of Commerce
National Technical Information Service
NTIS.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/2-80-081		PB 80 203623

4. TITLE AND SUBTITLE	5. REPORT DATE
EVALUATION OF AMMONIA "FIXATION" COMPONENTS IN ACTUAL REFINERY SOUR WATERS	May 1980 issuing date
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Committee on Refinery Environmental Control	API Publication 954
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
American Petroleum Institute 2101 L. Street Northwest Washington, D.C. 20037	1BB610 (C33B1B)
	11. CONTRACT/GRANT NO.
	R 804364010
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Robert S. Kerr Environmental Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Ada, Oklahoma 74820	Final 3/76 - 11/77
	14. SPONSORING AGENCY CODE
	EPA/600/15

15. SUPPLEMENTARY NOTES

American Petroleum Institute project officer: Ron Gantz

16. ABSTRACT

High ammonia concentrations (fixed ammonia) in stripped sour waters from petroleum refining are caused by weak organic acids and both weak and strong sulfur acids. The sulfur acids result from oxidation of sulfides present in sour water. Fixed ammonia can be eliminated by adding its molar equivalent of caustic to the top of the stripping column. Caustic addition does not interfere with sulfide removal.

Recommended techniques for measuring cyanide and sulfide concentrations in sour waters are inadequate. Ammonia concentration may be overestimated when the recommended procedure is used because ammonia can be generated from organic nitrogen compounds which are present in refinery sour waters.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Ammonia Phenol Hydrogen sulfide Stripping Hydrogen cyanide Organic acids Inorganic acids	Sour water stripping Ammonia fixation Sulfide oxidation Cyanide measurement Ammonia measurement Sulfide measurement	7A, 7B, 7C, 13B

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
Release unlimited	Unclassified	
	20. SECURITY CLASS (This page)	22. PRICE
	Unclassified	

EPA Form 2220-1 (9-73)

United States
Environmental Protection
Agency

Robert S. Kerr Environmental Research
Laboratory
Ada OK 74820

EPA-600/2-80-081
May 1980

PB80-203623

Research and Development

EPA

Evaluation of Ammonia "Fixation" Components in Actual Refinery Sour Waters

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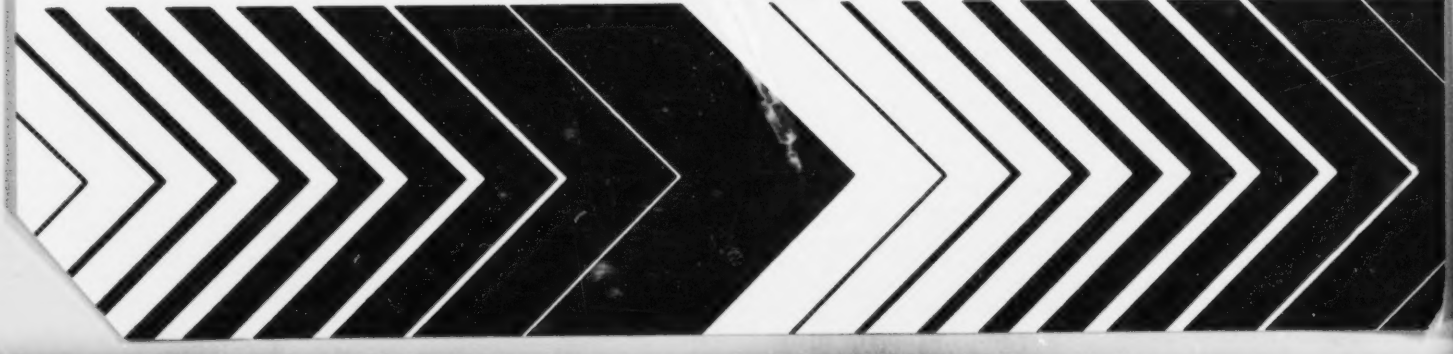

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EPA-600/2-80-081
May 1980

EVALUATION OF AMMONIA "FIXATION" COMPONENTS IN ACTUAL REFINERY SOUR WATERS

by

American Petroleum Institute
Committee on Refinery Environmental Control
Washington, D.C. 20037

Grant No. R 804364010

Project Officer

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This study was conducted by SRI International
under subcontract to the American Petroleum Institute,
Committee on Refinery Environmental Control

ROBERT S. KERR ENVIRONMENTAL RESEARCH LABORATORY
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ADA, OKLAHOMA 74820

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FOREWORD

The Environmental Protection Agency was established to coordinate administration of the major Federal programs designed to protect the quality of our environment.

An important part of the Agency's effort involves the search for information about environmental problems, management techniques and new technologies through which optimum use of the Nation'a land and water resources can be assured and the threat pollution poses to the welfare of the American people can be minimized. EPA's Office of Research and Development conducts this search through a nationwide network of research facilities.

As one of these facilities, the Robert S. Kerr Environmental Research Laboratory is responsible for the management of programs to: (a) investigate the nature, transport, fate and management of pollutants in ground water; (b) develop and demonstrate methods for treating wastewaters with soil and other natural systems; (c) develop and demonstrate pollution control technologies for irrigation return flows; (d) develop and demonstrate pollution control technologies for animal production wastes; (e) develop and demonstrate technologies to prevent, control, or abate pollution from the petroleum refining and petrochemical industries; and (f) develop and demonstrate technologies to manage pollution resulting from combinations of industrial wastewaters or industrial/municipal wastewaters.

The aquatic organism toxicity of ammonium compounds in solution is attributable to the un-ionized portion--ammonia per se. The upper limit recommended for ammonia by "Water Quality Criteria - 1972" is only 0.2 mg/1. Since ammonia is a common component of many industrial process effluents, high removal efficiencies are necessary to control effluent concentrations at acceptable levels. This report contains the findings of a study to determine the technology for increasing ammonia removal efficiency of the sour water scrubber process, a major source of the ammonia content of refinery wastewater streams. Economics of ammonia removal technology up to 99 percent efficiency are discussed.

William C. Galegar

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Director
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ABSTRACT

Ammonia fixation is a term used to describe the occurrence of ammonia in stripped sour waters (SSW) that is resistant to removal by means of additional steam. Samples of refinery SSW were analyzed for organic components, oxidized sulfur compounds, and heavy metals to determine the cause of ammonia fixation during stripping. The heavy metals levels measured were too low to be causes of fixation. However, acidic materials were identified that would cause fixation. These acids included thiosulfuric acid, thiocyanic acid, and weak organic acids. In some SSW, ammonia is synthesized during analysis, resulting in an apparent nonstrippable residual ammonia.

The amount of ammonia fixation that will occur with a particular sour water can be predicted by a potentiometric titration. Fixation can also be predicted by batch stripping using nitrogen gas until the pH of the stripped water reaches 6.

Laboratory experiments showed that fixed ammonia can be freed by adding caustic to the sour water stripper. The most effective place to add caustic is high in the stripping tower. The amount of caustic required to free fixed ammonia has no effect on sulfide stripping.

Laboratory stripping experiments were used to demonstrate that caustic can substitute for steam in producing a SSW with low levels of ammonia. An economic analysis showed that caustic use is only warranted when very high ammonia removal (>97%) is required, and that the economic optimum steam and caustic usage would degrade sulfide removal performance.

Laboratory stripping experiments could not be used to study the behavior of cyanides during stripping of actual refinery sour waters. Cyanide measurements were accurate in artificially prepared sour waters, and studies with these artificial sour waters showed that average refinery stripper operation could remove simple cyanide and convert some cyanide to thiocyanate. Metal-complexed cyanide was largely unaffected by stripping.

This report was submitted by SRI International to the American Petroleum Institute in partial fulfillment of Grant No. R 804364010 under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from March 15, 1976, to March 1977, and work was completed as of November 30, 1977.

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ACKNOWLEDGMENT

This work was performed by David C. Bomberger and James H. Smith at SRI International, Menlo Park, California under a subcontract to the Committee on Refinery Environmental Control (CREC) of the American Petroleum Institute. The U.S. Environmental Protection Agency funded the project on a cost sharing basis with the API with Grant No. R 804364010.

SECTION 1

INTRODUCTION

Since 1971 the American Petroleum Institute has been investigating the problem of stripping-resistant, or fixed, ammonia in sour waters generated by refinery processing operations. Surveys of refinery operations conducted in 1972 indicated that the problem was severe enough to justify a research program to develop improvements in stripping technology and stripper design. The research program has concentrated on identifying the causes of ammonia fixation and on developing new equilibrium data for the NH_3-H_2S-H_2O system in order to provide an expanded data base for stripper design.

An experimental study of sour water stripping conducted in 1974 (Bechtel, 1976) concluded that ammonia fixation was probably caused by acidic material in the sour water. No positive identification of the acidic material was made in the 1974 study. In March 1976 an experimental study of ammonia fixation was initiated to answer some questions raised by previous studies and to study stripper operating procedures designed to eliminate ammonia fixation. The five principal objectives of the study were:

1. Identify the organic and inorganic compounds present in sour waters which cause ammonia fixation.
2. Identify factors in refinery processing operations or feedstocks that may be responsible for ammonia fixation.
3. Investigate in the laboratory the suitability of caustic addition and pH control during stripping for eliminating ammonia fixation.
4. Identify the cyanide compounds present in refinery sour waters and determine their behavior during stripping.
5. Determine if there is any incentive for substituting caustic for steam during stripping of sour waters that do not have high ammonia residuals.

Stripped sour waters from eight refineries were analyzed to determine the composition of refinery sour water. The refineries were chosen to include plants processing California, Middle East, Gulf Coast and Mid-Continent crudes. Sour waters from several of these refineries were stripped in a laboratory scale stripping column to fulfill the other objectives of the program.

SECTION 2

CONCLUSIONS

SOUR WATER COMPOSITION AND AMMONIA FIXATION

(1) In the sour waters examined, ammonia fixation appears to be caused by weak organic acids and acidic oxidized sulfur compounds. Organic acids were an important acidic component of the sour waters studied. Ammonia-metal complexes were not a factor in the sour waters studied.

(2) The sample of 8 refineries was not large enough to identify the source of the acidic compounds. Neither the organic acids nor the oxidized sulfur compounds could be firmly associated with a particular crude source or crude processing operation.

(3) The amount of ammonia fixation can be measured in unstripped sour water by batch stripping tests where nitrogen and steam are used to strip ammonia and sulfide, or by acid-base titrations of sulfide-free stripped sour water.

(4) The distillation procedure for ammonia concentration measurement gave high readings for some sour waters.

(5) Some ammonia may actually be synthesized during analysis. Ammonia measurement by Nesslerization and any use of distillation pH values greater than 7.4 should be avoided.

(6) Phenol, cresols, and other aromatics with molecular weights less that 300 constitute a substantial fraction of the organic material found in sour waters.

ELIMINATING AMMONIA FIXATION

(7) Ammonia fixation can be eliminated by adding caustic to a sour water stripper. The amount of caustic required is the molar equivalent of the fixed ammonia.

(8) The optimum place to apply caustic to free the fixed ammonia is at the top of the column. Even when 10% excess is added to the top tray, sulfide stripping is not inhibited.

(9) In terms of ammonia removal efficiency, multiple-point caustic injection is inferior to single-point injection.

(10) Caustic can be economically substituted for steam during stripping of sour waters with no fixed ammonia. Caustic substitution for steam is optimum when very high ammonia removal efficiencies are required, but the level of ammonia removal at which caustic addition becomes attractive depends on the price of steam relative to caustic. For the sour water studied the following results were obtained:

Price of Steam	Price of Caustic	Ammonia Removal Efficiency where Caustic Addition Becomes Economically Attractive
$3.00/1000 lb*	$0.07/lb	97%
0.50/1000 lb	$0.11/lb	99%

When fixed ammonia is not present, caustic addition does degrade sulfide removal efficiency.

CYANIDES

(11) Tentative ASTM methods A and F for measuring cyanide compounds are unsatisfactory for the sour waters used in this investigation.

(12) Metal-complexed cyanides are by and large unaffected by conditions in a stripping column. A small percentage of these break down to simple cyanide, which is stripped.

(13) Some CN^- was converted to SCN^- during cyanide stripping.

(14) Simple cyanides such as HCN, KCN, NaCN appear to be readily stripped under the conditions normally encountered in sour water strippers, even though cyanide stripping experiments with buffered solutions show cyanide stripping is severely impaired at pH 9.

*1000 lb = 454 kg. See page H-2 for factors used to convert English units to metric units.

HYDROGEN SULFIDE

(15) The methylene blue test used for sulfide concentration measurement is not reproducible and it is heavily dependent on analyst technique.

ORGANIC ANALYSIS

(16) A simple method for measuring phenol and cresol concentrations in sour waters was developed. The procedure utilizes direct analysis of the sour water sample by high pressure liquid chromatography. This method could be readily adapted to measuring aromatic carboxilic acids.

(17) XAD* resins can be used to separate the organic compounds in sour water into basic, phenolic and acid fractions. Separations using XAD resins are much sharper and quantitative than separations using solvent extractions.

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*Rohm and Haas Company.

SECTION 3

RECOMMENDATIONS

(1) Procedures using XAD resins and high-pressure liquid chromatography show promise as a means of separating phenols from organic acids so that the acids in sour water can be identified and measured. Work in this area should be continued.

(2) Analytical procedures for measuring cyanides in sour waters are inadequate. Ongoing programs to validate cyanide measurement methods should continue.

(3) Nitrogen compounds that hydrolyze to form ammonia appear to be present in several of the sour waters tested. The compounds could not be identified because they could not be separated from phenolic compounds. Separation procedures using XAD resins should be developed.

(4) Alternate hydrogen sulfide measurement procedures should be investigated.

(5) Additional sour waters with high ammonia residuals should be analyzed by titration and batch stripping tests to validate the relationships identified in this study.

(6) A larger sample of refineries would be required to identify crude or processing operation influences on sour water composition and ammonia fixation. Any future study should analyze sour waters produced by individual processing units rather than the composite sour water from the entire refinery.

SECTION 4

BACKGROUND

Refinery sour waters contain thousands of parts per million (ppm) of sulfides and ammonia and hundreds of ppm of various organic compounds. Sulfides and ammonia are generated by many process operations and show up in distillation condensates and scrubbing streams. Distillation tower overhead condensate often contains water that entered with the feed or was introduced as a vapor phase diluent. Because of high vapor concentrations and water solubilities, sulfide and ammonia in the feed streams are concentrated in the condensed water. Operations that generate sour condensates include crude distillation and residual vacuum distillations as well as distillations following operations such as coking, gas oil hydrotreating, and cracking. Additional sour waters result from neutralized caustic scrubbing streams that are used to remove sulfide and sulfur compounds as well as phenols from cracked and hydro-treated hydrocarbon streams.

The various sour water streams are collected and steam-stripped to remove sulfide and ammonia. Stripped sour water is amenable to biological treatment and is usually mixed with other aqueous effluents on their way to treatment facilities. The ammonia level in stripped sour water can be a major determinant of whether the treated combined effluent meets discharge requirements.

Sulfide removal from sour water is accomplished readily by stripping. Ammonia removal is a more difficult problem. Laboratory experiments and theoretical calculations have shown that in aqueous solutions of phenol, hydrogen sulfide, and ammonia, almost complete removal of both sulfide and ammonia is possible. Some refineries actually achieve this level of sulfide and ammonia removal. Other refineries achieve good sulfide removals but cannot achieve ammonia bottoms values below 100 ppm. This ammonia often cannot be removed by increasing stripping steam rates. There are a number of possible explanations for this residual or fixed ammonia. In some cases, it can be related to acidic materials that tie up ammonia as NH_4^+. Acids containing sulfur and oxygen were implicated in laboratory work conducted for the API by Bechtel Corporation (1976). The Bechtel study also suggested that carboxylic acids such as fatty acids and naphthenic acid were involved, but these compounds were not identified positively by chemical analysis. The current project demonstrated, however, that when acidic compounds are responsible for retention of ammonia, caustic addition to the sour water can reduce or eliminate ammonia residuals.

In some cases, however, it is more difficult to identify the cause of ammonia retention, because pH adjustment does not release all of the ammonia (Dobrzanski and Thompson, 1974). A possible explanation is heavy metals that form complexes with ammonia. Alternatively, ammonia residuals may be apparent only because they are caused by interferences during the analytical procedure.

Metal-ammonia complexes are not strong relative to cyanide complexes as can be seen by considering copper complexes as an example:

$$Cu(NH_3)_4^{2+} \rightleftharpoons Cu^{2+} + 4\ NH_3;\ K_d \cong 10^{-11}$$

$$Cu(CN)_4^{2-} \rightleftharpoons Cu^{2+} + 4\ CN^-;\ K_d \cong 10^{-25}$$

Metals form cyanide complexes preferentially and would be available to form ammonia complexes only when the metals are present in excess of the amount required for cyanide complexes.

Interference in analysis of ammonia may be a more plausible explanation than formation of metal complexes. Organic acids, aldehydes, ketones, and amines interfere with the direct Nesslerization test because they react with the reagents. Nesslerization after distillation is subject to the same interferences because some of the volatile compounds can distill over with the ammonia. Ammonia determinations by titration are also subject to positive interference by basic organic nitrogen compounds. Some compounds, such as urea, hydrolyze to form ammonia under the distillation conditions (Hoffman, 1976). A complete understanding of ammonia retention (apparent or real) requires identification of acidic compounds and the various interfering substances.

In cases where ammonia removal can be improved by pH control, the proper place to introduce a base into the stripper has been a point of controversy. Introduction of caustic in the tower top is optimum for ammonia removal since it will increase ammonia volatility in every stripping stage. However, this is the least optimum point for sulfide removal since sulfide volatility is decreased in all stripping stages. It has been suggested that some point in the middle of the column would be a reasonable compromise.

Once an appropriate caustic addition strategy has been established, it seems proper to consider whether adding caustic would permit good stripping of both sulfide and ammonia with less steam than is used in

common practice. The incentive for considering this alternative is the increasing unit cost of steam. Although in the long run caustic price will also rise when steam cost increases, there may be some lag due to market forces, since much caustic is produced as a coproduct of chlorine manufacture. Stripping response will be a complex function of steam rate, caustic addition rate, and the number of equilibrium stages in the column. Sour water organics such as weak acids will also affect stripping response. When adequate computational models are available, the incentive for caustic-steam substitution can be studied without resort to experiment, but experiments are required at present.

Some cyanide compounds are extremely toxic. Their fate during stripping is important if the stripped sour waters are discharged to receiving streams. Free cyanide may not be the most abundant cyanide compound present in sour waters since many metals form strong complexes with cyanide. Metals such as copper catalyze reactions that convert cyanide to cyanate. Because the possibilities for cyanide reactions are numerous, it seems most reasonable to determine how cyanides react under stripping conditions by experiment.

FUNDAMENTALS OF STRIPPING

Since several phases of this investigation involve steam stripping of both refinery and artificial sour waters, it is appropriate to reveiw the fundamentals of stripper operation. A simple stripper of N equilibrium stages with no reflux can be modeled mathematically by the expression [Smith (1963)].

$$f = \frac{1 - S}{1 - S^{N+1}}, \qquad (1)$$

where f is the fraction of a component in the feed that remains in the bottoms. S is the stripping factor K(V/L) when V is the vapor rate, and L is the liquid rate in the column. K is the liquid-vapor partition coefficient for the component being considered. This simple model assumes that liquid and vapor rates are constant along with K.

A sour water stripper has approximately constant L and V when stripper feed is preheated, with L being the feed rate and V the steam rate, but K need not be constant, principally because ionic equilibrium between the species H_2S - HS^-, NH_3 - NH_4^+, and H^+ affects vapor pressure.

In the case of ammonia, we express ammonia liquid-vapor equilibrium by

$$y_{NH_3} = K'_{NH_3} \, x_{NH_3} \qquad (2)$$

where x and y are mole fractions of NH_3 in the liquid and vapor phases and K'_{NH_3} is the liquid-vapor partition coefficient. K'_{NH_3} is a constant that is only a weak function of NH_3 concentration. NH_3 is in equilibrium with NH_4^+, and the relative amounts of the two species are determined by the ionic equilibrium constant k_N:

$$k_N = \frac{[NH_4^+]}{[NH_3]\,[H^+]} \quad , \qquad (3)$$

where $[H^+]$ is the hydrogen ion concentration. Because of this equilibrium, Equation (2) can be rewritten as

$$y_{NH_3} = K'_{NH_3} \left[\frac{1}{1 + k_N\,[H^+]}\right] x_N \quad . \qquad (4)$$

If we identify $K'_{NH_3} / (1 + k_N\,[H^+])$ as K_N, Equation (4) becomes

$$y_N = K_N \, x_N \quad , \qquad (5)$$

where y_N and x_N represent the mole fraction of the sum of both ammonia species, NH_3 and NH_4^+. This sum is measurable as ammonia nitrogen (NH_3-N). In Equation (5), liquid-vapor equilibrium has been redefined in terms of the concentrations measured by the analytical procedures normally used in a laboratory. Relationship (2) or (5) holds even when other ionic species are present in the system.* The only impact of these other species is to change k_N by ionic strength effects. For ammonia, it is K_N, the liquid-vapor partition coefficient for ammonia nitrogen (which is a strong-function of only pH) that becomes the appropriate partition coefficient to use in the stripping factor, S.

*Chemical reactions with carbonate and bicarbonate to form urea and carbamide are neglected in this development.

In a similar manner, we can include the pH effects on the partitioning of sulfide between liquid and vapor by including the equilibrium between sulfide species, $k_S = [H^+]\,[HS^-] / [H_2S]$. This gives

$$y_S = K'_{H_2S} \left(\frac{[H^+]}{k_S + [H^+]} \right) x_S \qquad (6)$$

and

$$y_S = K_S x_S \quad , \qquad (7)$$

where y_S and x_S represent the mole fraction of the sum of the species HS^- and H_2S, identified as sulfide sulfur (H_2S-S). K_S is a function of pH and describes sulfide vapor-liquid equilibrium in terms of the variable measured by analytical techniques. It is the appropriate partition coefficient to use in a stripping factor S for sulfide sulfur.

Figure 1 illustrates the effect of pH on the ionic equilibiium of H_2S and NH_3. When this behavior is combined with Henry's Law constants (Wilson, 1976), for both species, the result is Figure 2. These plots show liquid-vapor partition coefficients K_N and K_S over the entire pH range at a temperature of 100°C. Figure 2 shows that H_2S-S and NH_3-N are both volatile over the pH range 6 to 11. Below pH 6, only H_2S-S is volatile; above pH 11, only NH_3-N is volatile. In the pH range where both are volatile, H_2S-S is the more volatile from pH 6 to pH 9, and NH_3-N is the more volatile above pH 9. It is important to note that NH_3-N has a constant K_N for all pH values above 10.

Both Figures 1 and 2 are shown in terms of the pH at conditions in the tower. These figures would look different if pH at 25°C were used because of the way temperature effects K_N, K_S, and K_W, where K_W is the equilibrium constant for the reaction $H_2O \rightleftarrows H^+ + OH^-$. When a solution of H_2S and NH_3 at 100°C is cooled, the concentration of H^+ decreases as the temperature falls. The pH of the solution increases. The magnitude of this pH effect depends on the concentrations of H_2S and NH_3 present and in general is larger when concentrations are large. Thus at concentrations typical of sour water feed, the pH at 25°C could be almost 2 units higher than the pH at 100°C. For stripped wour water with low concentrations of NH_3 and H_2S, the change in pH with temperature would be small.

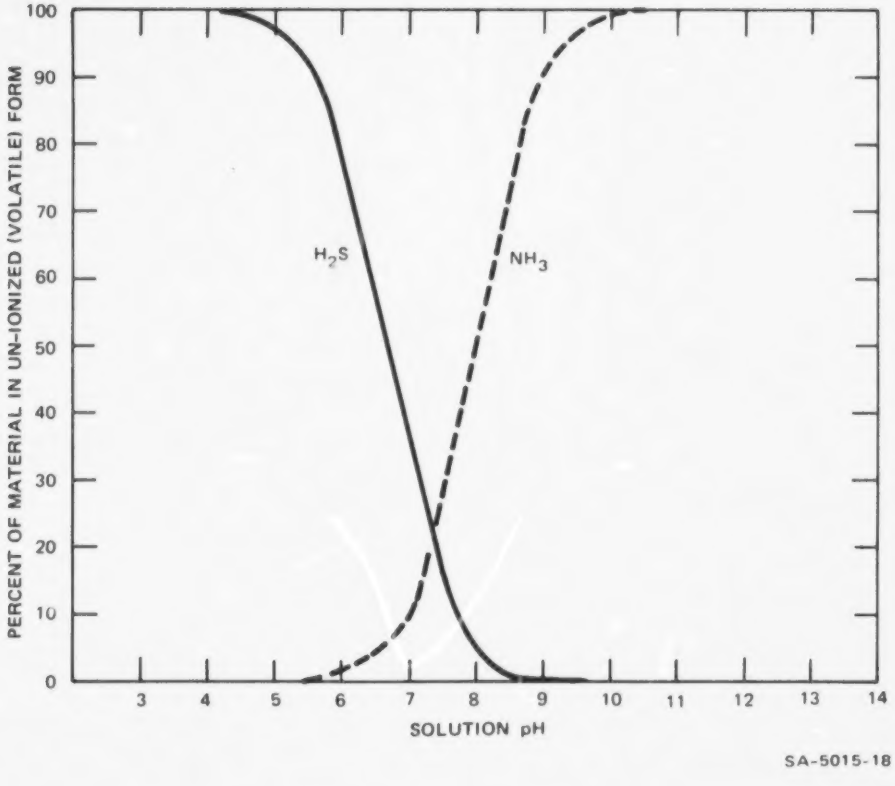

Figure 1. Ammonia and sulfide ionization as a function of solution pH at 100°C (Wilson, 1976).

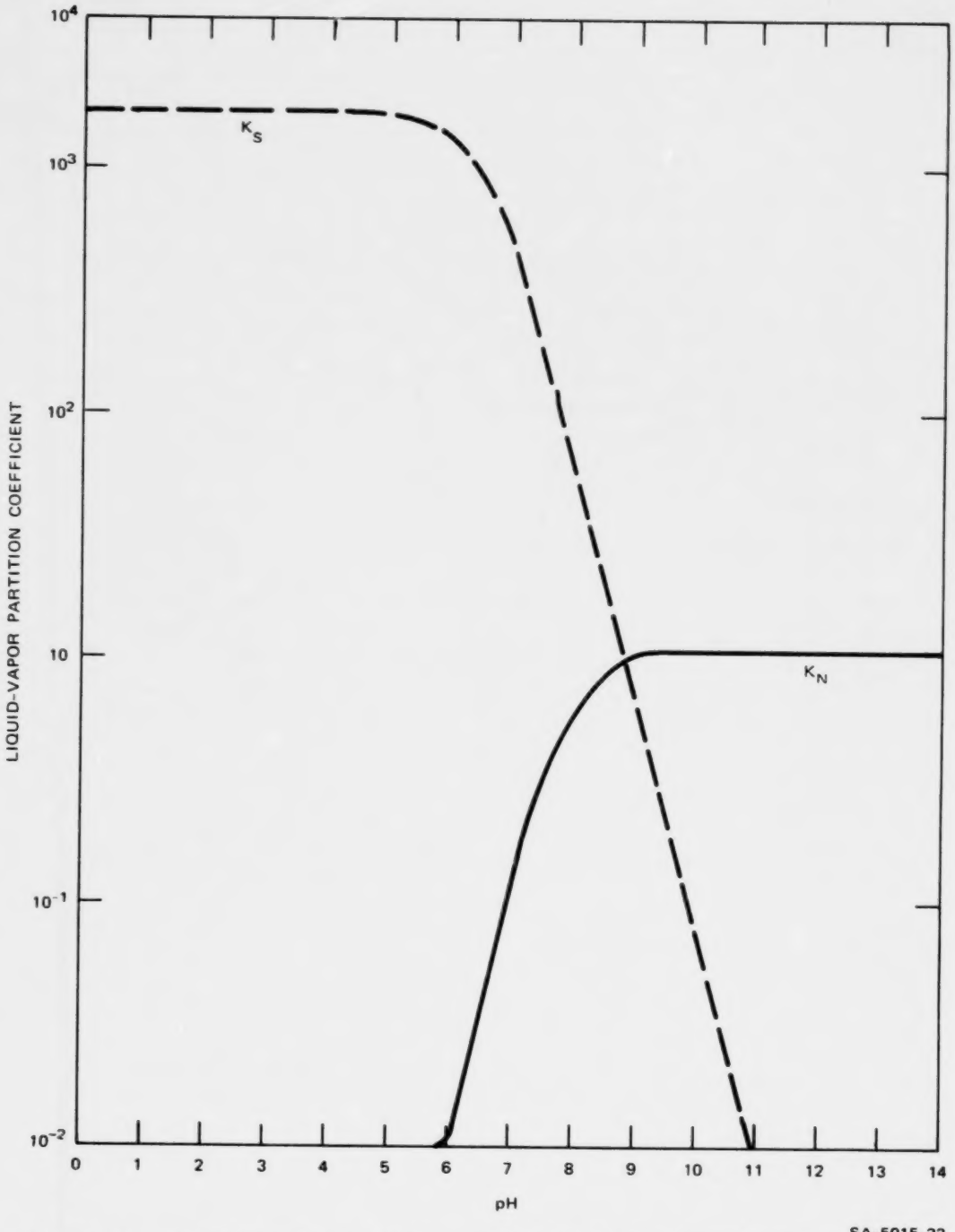

Figure 2. Liquid-vapor partition coefficients for ammonia-nitrogen and sulfide-sulfur as a function of pH at 100°C and 1 atmosphere total pressure.

The result of the pH behavior of K_N and K_S (illustrated in Figure 2) is that any sour water containing only ammonia, sulfide, and compounds that do not effect pH would leave a stripper at a pH of about 9, regardless of feed ammonia and sulfide composition. This pH of 9 will be referred to often in the rest of this report. It is important to realize that this pH is dependent on the choice of equilibrium and Henry's Law constants. It is also a function of stripper temperature. An actual stripper may converge to a different pH, but this difference does not affect the principles involved. A feed containing a molar excess of sulfide would start out acidic. Under this condition of $K_S > K_N$, the feed would lose a higher percentage of its sulfide than its ammonia on each stripping stage. As the feed progressed down the stripping column, it would become more basic until it approached a pH of about 9 where $K_S = K_N$, and it would lose the same percentage of both components on each stripping stage below this point in the column. This equal percentage loss would keep concentration ratios, and thus pH, constant during the rest of the feed's passage through the stripper.

A feed that starts with an excess of ammonia would lose ammonia more rapidly than sulfide and approach a constant pH of 9 from the basic side. In cases where steam rates are high, excess sulfide or ammonia might be lost quite rapidly and for most of the stripper $K_S = K_N$ = constant. Equation (1) could be used to give an approximate model of stripping behavior. From Figure 2 we see that at pH 9, $K_S = K_N = 10$. For a stripper using 1.5 lb of steam per gallon of tower feed,* $S \cong 2$ and

$$f = \frac{1}{2^{N+1} - 1} \quad ,$$

The presence of species that have an effect on solution pH can influence the operation of a stripper in a number of ways. Except for cases where these materials are present in large amounts, we would expect the effect to be strong only in the bottom of the column where their relative molar quantities are high. Consider, for example, a sour water feed of 10,000 ppm H_2S and 7,500 ppm NH_3, which has a pH of about 9 (Beychok, 1967). The concentrations are equivalent to 294 meq/ℓ H_2S-S and 441 meq/ℓ NH_3-N. If this sour water also contained 500 ppm TOC from benzoic acid (733 mg/ℓ benzoic acid), the acid would represent only 6 meq/ℓ, or less than 2% of the H_2S-S equivalents present. Under these circumstances, the benzoic acid would have only a very small effect on pH and hence the volatility of ammonia or sulfide in the top of the column. Toward the bottom of the column, however, after most of the sulfide and ammonia have been stripped, the benzoic acid could

*1.5 lb/gal = 179.7 kg/m^3. See p. 109 for conversion of English units to metric units.

represent an important ionizable species. The column bottoms would be acidic, rather than having a pH of near 9 as expected. It can be shown that when the moles of ammonia nitrogen present are equal to the moles of benzoic acid present, the pH of the solution falls below 6. From Figure 2 it can be seen that under these circumstances ammonia is no longer volatile; it has been fixed.

If a basic material like sodium hydroxide is present in small amounts, it also would not affect the pH in the top of the column. Near the bottom of the column, however, where ammonia and sulfide concentrations are low, the basic material would be an important component of the sour water and would cause the pH to raise above the level of 9. If sufficient base were present to raise the column pH above 11, sulfide would become nonvolatile or fixed.

It is important to notice that the point in the column where ammonia and sulfide levels become low enough to permit small amounts of acids and bases to affect the pH is strongly dependent on the steam rate. With high steam rates, low ammonia and sulfide levels will be achieved high in the column. With low steam rates, acids and bases will only be able to affect the pH near the column bottom.

SECTION 5

ANALYTICAL PROCEDURES

This section discusses the analyses of sulfide, ammonia, and cyanide, which significantly affected the results of this study. The routine analytical methods, including those of heavy metals and alkaline earth elements, all sulfur compounds, and nitrogen compounds, are included in Appendix A.

SULFIDE DETERMINATION

Sulfides proved to be the most difficult sulfur compounds to measure. Preliminary analyses using sour waters indicated that the methylene blue procedure described in Standard Methods (American Public Health Association, 1976) was reproducible and accurate. Known amounts of sulfide added to sour waters could be quantitatively recovered. Measurements of sulfide levels in refinery stripped sour waters were made by adding the color reagents to diluted samples. Later in the project it was found that measurements of low sulfide concentrations in laboratory stripped sour waters could not be made by direct addition of the color reagents to diluted samples. At low sulfide levels (10 ppm), some organic material in the sour water interferes with proper color development. At times it looked as though the methylene blue dye was being adsorbed by colloidal organic material that was present in our samples.

On the basis of this finding, we suspect that our measurements on refinery stripped samples may have underestimated the sulfide levels. The procedure that evolved for laboratory stripped samples entailed precipitation of the sulfide with cadmium hydroxide to separate the sulfide from the interference. Cadmium sulfide was removed from the sample by centrifugation.

Even with interferences removed, the method is not entirely satisfactory because it is too dependent on analyst technique. The timing of reagent addition and the amount of agitation used while adding reagents has a profound effect on the ultimate color development.

On the basis of duplicate analysis of laboratory stripped bottoms, we estimate that when concentrations were around 5 ppm the reproducibility was ± 1 ppm. At 100 ppm the reproducibility was ± 16 ppm.

For every stripping run the sulfide level in the feed was measured. Feed levels were on the order of 3000 ppm and our reproducibility was ± 10%.

The details of the method are described in Appendix A.

AMMONIA DETERMINATIONS

Ammonia was measured with an ammonia ion-specific electrode (Orion Research, Ammonia Electrode 95-10). All determinations with this electrode require that the solution measured be adjusted to a pH > 11 to convert all ammonia to the un-ionized form. Various experiments were conducted to determine what sample pretreatment was required to achieve accurate and precise measurements with the electrode, and to compare electrode results with alternate ammonia measurement procedures.

The major interferences claimed for the ammonia electrode* are:

- Mercury ions that form strong complexes with ammonia
- Volatile organic amines
- Wetting agents such as organic acids and phenols.

The first interference could not be a problem because no mercury was detected in any of the sour waters used in this study. Volatile amines are a very unlikely interference in stripped sour waters, although they may be present in the unstripped sour waters. The major interference of concern was organic acids and phenols, components that would be present in both stripped and unstripped sour water.

Table 1 contains a summary of a series of tests used to determine the suitability of various procedures using the Orion ammonia electrode. The table shows that with actual refinery-stripped sour water, the results of spike recoveries vary.

The following procedures were investigated:

(1) Direct determinations using an Orion model 95-10 ammonia electrode, including some measurements made after removal of organic acids and phenols by ether extraction.

(2) Ammonia electrode determinations of condensate collected from a sample buffered to pH 9.5 during distillation. This method is described in an EPA manual (1976). Phenols as a class are not very volatile at any pH. Organic acids are essentially non-volatile at pH 9.5. Therefore, the distillate or condensate would not contain either of these materials.

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*Instruction Manual, Ammonia Electrode 95-10, Orion Research.

TABLE 1. AMMONIA DETERMINATIONS WITH THE AMMONIA ELECTRODE--SPIKE RECOVERIES

Ammonia Addition to 25 cc of Refinery A Stripped Bottoms Diluted to 100 cc with Water and Dechlorinating Agent	mg/ℓ NH_3-N in Diluted Sample			
	Direct Measurement with Ammonia Electrode	Direct Measurement with Ammonia Electrode After Organic Acids Removed*	Measurement with Ammonia Electrode after Distillation at pH 9.5	pH >11
+ 0 mg/ℓ NH_3-N	3	4	6	13
	3	4	6	
+ 10 mg/ℓ NH_3-N	13		16	
	13		15.5	
+ 20 mg/ℓ NH_3-N	22	22	23.5	
	23	23	25	
+ 30 mg/ℓ NH_3-N	32			
+ 40 mg/ℓ NH_3-N	41	39	41	
		41	42.5	

*Multiple extraction with ether under acidic conditions.

(3) Ammonia electrode determinations of condensate collected from a sample adjusted to pH > 11 before distillation.

Double entries in Table 1 represent duplicate determinations from the same sample. The duplicate determinations suggest that the precision of the technique is ± 1 ppm.

The data show that at sample ammonia levels below 30 ppm, good spike recoveries are obtained when determinations are made with the ammonia electrode in the condensate collected during distillation at pH 9.5. The good spike recoveries indicate that if the total amount of ammonia introduced into the distillation apparatus is carefully restricted, pH 9.5 is adequate to give 100% ammonia recovery. For the unspiked sample, determinations were made in condensate obtained from distillation at pH 9.5 and pH 11. Recovery is complete at pH 9.5, and reproducibility is ± 1 ppm. The 6 ppm increase in ammonia seen when the distillation pH is adjusted from 9.5 to 11 indicates that free ammonia is generated from some nitrogen-containing material present in the stripped sour water.

The data also show that good spike recoveries are obtained when the ammonia electrode is used directly in the sample without distillation. There is no apparent effect of concentration on spike recoveries.

Comparison of the results obtained after extraction of organic acids, phenols, and other organic compounds with results obtained from untreated samples indicates that with this particular stripped sour water, organic acids do not interfere with the performance of the ammonia electrode.

In summary, the data in Table 1 suggest that:

(1) Spike recoveries in sour water indicate that direct determinations with the ammonia electrode without distillation are accurate.

(2) Distillation pretreatment is unnecessary and is harmful. Certainly, distillation at pH greater than 9.5 must be avoided. Standard Methods (1976) emphasize the use of pH of 7.4 to reduce interferences.

(3) Organic acids and phenols did not interfere with determinations made with the ammonia electrode.

EPA-approved methods for ammonia determination do not permit using the ammonia electrode except after distillation. Therefore, additional studies using several stripped sour waters were conducted to determine the effects of distillation. In addition, ammonia electrode determinations were compared to Nesslerization results. The data are shown in Table 2.

TABLE 2. DETERMINATION OF THE EFFECT OF DISTILLATION PRETREATMENT AND DIFFERENT FINISHES ON AMMONIA MEASUREMENTS (ppm)

Refinery Sample	Procedure	Sample Number A1	A2	F1	G1
TKN		192	242	197	52
NH_3-N	Direct determination with ammonia electrode	14	11	90	26
NH_3-N	EPA distillation at pH 9.5; Ammonia electrode finish	24	30,26*	88,86*	30,30*
	Nessler Finish	--	33,28*	112,109*	40,35*
	TKN finish	--	--	90,85*	34,30*
NH_3-N	Distillation at pH 11; Ammonia electrode finish	--	53,51*	--	--
	Nessler finish	56†	55,50*	--	--

*Duplicate determinations of the same sample.

†Analysis supplied by refinery.

Multiple entries are from duplicate determinations. Analysis of the duplicates suggest that the reproducibility of our analysis was ± 2 ppm for this series of tests.

For samples F1 and G1 and ammonia concentration in the condensate from the EPA-approved distillation at pH 9.5 was measured by ammonia electrode, Nesslerization, and total Kjeldahl nitrogen (TKN).

(1) The agreement between the TKN and electrode methods is strong evidence that the electrode is accurately measuring ammonia concentration in the condensate.

(2) The agreement between the TKN and electrode methods indicates that samples F1 and G1 contain no volatile amines to interfere with electrode determinations.

(3) Nesslerization is a poor choice for ammonia measurements in sour waters. For both samples F1 and G1, the Nesslerization result is high, probably because of interference from organics such as ketones, aldehydes, or phenols.

Assuming that the electrode and TKN finishes are both correct, the ammonia concentrations determined after distillation for F1 and G1 are 87 ± 2 and 31 ± 2, respectively. The results can be summarized as follows:

	F1	G1
NH_3–N direct determination with ammonia electrode	90 ± 2	26 ± 2
NH_3–N determination after distillation at pH 9.5	87 ± 2	31 ± 2

The differences (for samples F1 and G1) between determinations with and without distillation are not significant. Two inferences were drawn from this result.

(1) It is another confirmation of the accuracy of direct measurements of ammonia with the electrode without distillation pretreatment.

(2) It shows that distillation of these two samples at pH 9.5 does not generate ammonia.

It is important to compare the results for samples A1 and A2 with those for F1 and G1. If direct electrode determinations of ammonia in samples A1 and A2 (and F1 and G1 as well) are correct, the results in Table 2 show that free ammonia is being generated by the EPA distillation procedure for sample A1 and A2 but not for sample F1 and G1. Note the increase in ammonia generation when the pH is raised from 9.5 to 11.

It is also interesting to note that Nesslerization determinations after distillation agree with electrode determinations after distillation for samples A1 and A2. This is a sharp contrast to the results obtained with samples F1 and G1.

We feel that the conclusions to be drawn from these comparison studies are:

(1) Nesslerization should not be used to measure ammonia in sour waters.

(2) With some sour waters, the EPA distillation at pH 9.5 generates free ammonia, thus causing overestimation of ammonia concentrations.

(3) An ammonia measurement using a distillation at pH > 9.5 should not be used.

(4) Direct determination of ammonia with an ammonia electrode gives an accurate measurement of concentration for the sour waters.

Even though direct electrode determinations were the preferred technique for this study, electrode determinations after distillation at a pH of 9.5 were chosen as the method for the bulk of the experimental work in order to produce results that would be consistent with future regulatory procedures.

CYANIDE DETERMINATIONS

Total cyanide was measured using tentative ASTM Method A, and free cyanide was measured using tentative ASTM Method F. The validity of the procedures used in this study to measure cyanide is questionable. Free cyanide measurements sometimes gave higher results than a total cyanide measurement. Experiments to check the accuracy and precision of Method F (ASTM), which is purported to measure free cyanides, were performed in refinery sample A2 and in distilled water. The averages of duplicate measurements are shown in Table 3. The reproducibility was

TABLE 3. EXPERIMENTS TO DETERMINE ACCURACY OF CYANIDE MEASUREMENTS

Feed	CN^- (Method F)* (ppm)
Refinery sample A2	10.75
Refinery sample A2 + 50 ppm CN^-	55.00
Refinery sample A2 + 50 ppm CN^- from KSCN	10.15
Distilled water + 0.5 ppm CN^- from KCN	0.5
Distilled water + 1.0 ppm CN^- from KCN	1.0

*ASTM Method F is purported to measure only CN^- in solution. Metal-complexed cyanides and thiocyanate are not supposed to be detected by this procedure.

on the order of one percent. The accuracy, as determined from spike recoveries of added cyanide both in the distilled water and the sour water, appears excellent. The data also show that added thiocyanate does not interfere with the cyanide analysis.

In contrast to the above, cyanide measurements on eight sour water samples obtained from various refineries were generally unsatisfactory. These results are summarized in Table 4. The determinations for samples C1 through G1 were duplicated and showed good reproducibility, with measurements differing from the mean by no more than five percent. However, for refinery samples A2, C1, F1, and G1, the free cyanide determination exceeds the total cyanide determination by a significant amount, perhaps a result of some unknown interferences. It appears that we can measure cyanides reproducibly and accurately in distilled water but not in actual refinery samples.

TABLE 4. CYANIDE DETERMINATIONS IN REFINERY STRIPPED SOUR WATERS

Refinery Sample	Total Cyanide (ASTM Method A)* (ppm)	Free Cyanide (ASTM Method F)† (ppm)
A1	18.1	5.5
A2	0.6	10.7
B1	0.15	0.02
C1	0.51	2.34
	0.50	2.21
D1	4.62	4.44
	4.87	4.87
E1	10.17	0.06
	10.37	0.06
F1	1.37	9.83
	1.37	9.75
G1	0.02	1.19
	0.02	1.19

*Tentative ASTM Method A measures CN^- and most metal-complexed cyanide and is not supposed to measure thiocyanate.

†Tentative ASTM Method F measures CN^- only and is not supposed to measure thiocyanate.

SECTION 6

ANALYSIS OF REFINERY SOUR WATERS

Eight refineries with different crude slates and different refinery operations feeding the sour water strippers were sampled. Most of the stripped sour waters were collected under nitrogen and air-mailed to SRI International, where they were placed in a refrigerator at 4°C until analyzed. The samples were in transit from 2 to 5 days. Several refinery samples were collected by SRI staff and transported to our facilities on the same day.

Refinery A was sampled three times. The second sample was taken because the first had an unexpectedly low pH (the refinery adds caustic to the stripper). The third sample was acquired during the bench scale stripping phase of the program.. Refinery B's sample also yielded a pH that was too low, but it was not resampled because it contained very low levels of the materials of interest to this study.

NITROGEN AND SULFUR COMPOUNDS

Table 5 summarizes the results obtained from the eight refineries. The analysis on sample H1 is incomplete because it arrived late in the program. For all refineries except A and B, the two ammonia determinations (direct measurement with ammonia electrode and measurement after distillation) gave comparable results. Ammonia and TKN determinations were close in value, indicating that most of the nitrogen in these sour waters is ammonia. Only one, refinery A, stands out as having an excess of non-ammonia nitrogen. This refinery also shows significant generation of ammonia during the distillation part of the ammonia determination. Refinery A stripped sour water shows 14 ppm NH_3-N without distillation, 24 ppm NH_3-N after distillation at pH 9.5 (Table 5), and 52 ppm NH_3-N after distillation at pH 11 (Table 2).

All of the refineries except B and G show significant amounts of sulfur that is not sulfide. This can be seen by comparing the total sulfur measurements with the sulfide measurements. For Refineries A, C, and E, this extra sulfur is principally in the form of thiosulfate. Although the analysis for Refinery H is incomplete, the sulfur balance suggests that, with this refinery also, the non-sulfide sulfur is in the form of thiosulfate. Thiosulfate will behave as a strong acid. Therefore, thiosulfate is a more logical choice for the remaining sulfur in the sour water from Refinery H than is free sulfur, which is neutral.

TABLE 5. STRIPPED SOUR WATERS: ANALYSIS OF NITROGEN AND SULFUR SPECIES (ppm)

Refinery Sample	A1	A2	B1	C1	D1	E1	F1	G1	H1
pH	5.0	9.5	4.0	8.6	9.0	10.2	8.5	8.4	6.3
TKN*	192	242	6	208	80	1080	197	52	82
NH_3-N									
After distillation†	24	28	14	157	30	1075	87(110)**	30(38)	60
Direct‡	14	11	5	140	22	1000	90	26	60
Total sulfur	89[97]††	ND	0	297[231]	45[49]	229[276]	137[87]	5.5	115
H_2S-S	<1		ND	41	<1	116	13	<1	<1
SCN-S	ND			60	23	52	29	<0.1	4
S_2O_3-S	92			77	17	109	33	<2	ND
SO_2-S	5			1.6	1.5	2.1	12	<1	ND
Free sulfur-S	ND			52	6.4	<5	<5	<5	ND
Cyanide§									
Free	5.5	10.7	0.02	2.25	4.5	0.06	9.79	1.19	
Total	18	0.6	0.15	0.51	4.7	10.2	1.37	0.02	

Note: ND = Not determined.

*Total Kjeldahl Nitrogen.

†Ammonia measured with ammonia electrode in distillate using EPA approved distillation method at pH 9.5.

‡Ammonia measured with ammonia electrode directly in sample.

§Free cyanide measured using tentative ASTM method F. Total cyanide measured using tentative ASTM method A.

**( ) indicates Nessler finish

††[ ] indicates total from individual determinations.

The presence of these oxidized sulfur compounds indicates that the sour waters have been exposed to oxygen (Chen, 1971, 1972). Exposure during sampling was minimal, so we feel that the oxygen exposure occurred in the refineries, either from oxygen in the crude or exposure to air in the sour water system. The significance of the oxidized sulfur with respect to the ammonia levels in the sour water will be discussed in Section VII.

The cyanide measurements have been discussed previously in Section V, the only inference that can be drawn from them is that cyanides were present in most of the sour waters sampled.

HEAVY METALS AND ALKALI EARTH ELEMENTS

The results of metal analysis are shown in Table 6. The levels of heavy metals in all of the refinery sour waters are low enough to eliminate ammonia-metal complexes as a cause for ammonia fixation.

ORGANIC ANALYSIS OF STRIPPED SOUR WATERS

The objective of this phase of the project was to identify the organic compounds responsible for high residual ammonia in stripped sour water. We based our investigation on two general mechanisms that could lead to residual ammonia:

(1) Protonation of dissolved ammonia by weak organic acids, thereby reducing the ammonia vapor pressure.

(2) Presence of compounds in the stripped water that decompose to yield ammonia under the conditions of the ammonia test.

The ability of weak acids to neutralize ammonia depends on the pK_a of the acid. Representative pK_a values of selected acids are given in Table 7. Since the pK_a of ammonia (actually the pK of the conjugate acid of ammonia, the ammonium ion NH_4^+) is 9.25, both aliphatic and aromatic acids will protonate one mole of ammonia for every mole of acid. However, phenols are weaker acids and in a solution containing 1 equivalent of phenol and 1 equivalent of ammonia, only about 32% of the ammonia will be protonated. Thus, the reduction in the vapor pressure of the ammonia will not be large, and phenols should not significantly increase the residual ammonia.

TABLE 6. STRIPPED SOUR WATERS: INORGANIC ANALYSIS

Refinery Sample	A1	B1	C1	D1	E1	F1	G1	H1
Nonvolatile total solids (residual) (ppm)	1263	<10	191	313	20	59	13	ND
Composition of residual*(%)								
Na	40	ND	7.5	35	25	40	20	ND
Fe	0.5		1	0.75	0.2	1	1	
Ca	0.12		4	2.5	1.25	0.85	20	
Si	0.07		12.5	0.85	12	3	6	
Mg	0.025		25	1	0.5	0.15	2.5	
Al	0.02		0.07	0.07	0.08	0.4	0.25	
Ni	0.015		0.005	0.02	0.75	0.008	0.01	
Ba	0.003		--	--	0.004	--	--	
Cu	0.002		0.025	0.025	6	0.06	0.035	
Cr	0.001		0.04	0.02	0.006	0.01	0.015	
B	<0.01		0.75	0.12	2	0.015	0.15	
Mn	<0.001		0.04	0.007	0.06	0.05	0.07	
Pb	<0.005		<0.005	<0.005	<0.005	<0.005	0.01	
K	<0.5		2	2.5	1.5	1	2	
Sr	<0.01		0.15	0.04	0.008	0.015	0.02	
Metals in unfiltered sample								
Na (ppm)	500	1.3	11	92	2.5	18	2.5	ND
Fe (ppm)	6.3	0.0	0.0	1.4	0.0	0.0	0.0	
K (ppm)	2.2	<1.0	2	1.5	0.2	0.5	0.3	
Ca (ppm)	2.0	1.6	15	5.0	0.2	0.5	2.3	
Mg (ppm)	ND	ND	21	1.4	0.1	<0.05	0.6	
Cu (ppm)	ND	ND	ND	ND	1.4	ND	ND	
Ni (ppm)	ND	ND	ND	ND	0.0	ND	ND	

Note: ND = Not determined.

*Semiquantitative spectrographic reported as oxide.

TABLE 7. pK_a VALUES OF SELECTED ACIDS AT ROOM TEMPERATURE

Compound	pK_a
Acetic acid	4.75
Propionic acid	4.87
Hexanoic acid	4.88
Benzoic acid	4.19
1-Naphthoic acid	3.70
2-Naphthoic acid	4.17
Phenol	9.89
o-Cresol	10.20
m-Cresol	10.01
p-Cresol	10.17
Resorcinol	9.81
Hydrogen sulfide	6.9
Thiocyanic acid	4.0
Sulfurous acid	7.2
Thiosulfuric acid	1.7

Sources: Handbook of Chemistry and Physics, 54th Ed. Page (1953)

Our initial intention was to identify and quantify as many specific weak organic acids as possible in several stripped sour waters. However, we found that the organic material in the test samples was mainly phenolics, which made the analysis of organic acids very difficult within the allotted time and funds. Several attempts to identify organic acids were unsuccessful.

We were able, however, to measure the total concentration of weak acids (organic and inorganic) in the stripped sour waters by potentiometric titration. The inorganic acids were identified chemically, and the organic acids were back-calculated by difference. We also used the technique of gel permeation chromatography to measure the molecular weight distribution of the aromatic organic compounds in the stripped sour waters. The results obtained with both these measurement techniques are summarized below.

Total Organic Carbon

The total amount of organic material was determined by measuring the total organic carbon (TOC) and the loss on ignition. Most of the TOC measurements were made by a Beckman total carbon analyzer. The data for TOC and loss on ignition, as shown in Table 12, do not agree well. Since the data for loss on ignition are based on drying at 100°C followed by ignition in a muffle furnace, we believe that these measurements are less reliable than the TOC measurements, which require little sample pretreatment (acidification to remove CO_2) prior to analysis.

Total Weak Acids

The total amount of weak acids was measured by potentiometric titration, using a Brinkman Model E 306 automatic titration apparatus. An aliquot of stripped sour water (SSW) was titrated with 0.1 N HCl or 0.1 N NaOH. The pH of the solution was monitored as a function of the volume of titrant that had been added to the solution of SSW. The resulting titration curve was analyzed to determine the number of equivalents of weak acids ($pK_a \sim 5$) that were present in the solution. Titration curves for several SSW solutions are shown in Figures B-1, B-2, and B-3 in Appendix B. The weak acids are determined from the equivalents of titrant used between inflections on the titration curve between pH 9 and pH 3. The pK_a is the pH at the point where the amount of titrant used is ½ of the total weak acid equivalents.

The data are reported as milliequivalents of acid per liter of SSW (meq/liter). The titration procedure will only discriminate between different acids as a function of pK_a and not structure; weak inorganic acids, such as H_2S, thiocyanic, sulfurous, and carbonic would be titrated and reported as weak acids. However, data in Table 5 show that the sulfide concentrations in solutions titrated from the basic side were very low and would contribute very little weak acid. The high sulfide samples were titrated from the acid side and would have lost much of the sulfide during acidification. Therefore, within the precision of the results, sulfide probably does not contribute to the weak acids measured. The concentrations of the weak inorganic acids containing sulfur were reported in Table 5. There was no carbonic acid in any of the samples.

Separations by Polarity

XAD resins and extraction were evaluated as possible means of separating the organic material in SSW into four class fractions--amines, phenols, acids, and neutrals.

XAD resins are synthetic, hydrophobic, insoluble, crosslinked, polystyrene polymers. They have a macroreticular physical porosity and a high surface area. They adsorb nonionized species and do not retard ionized compounds in aqueous solutions. Organic acids having a $pK_a \sim 5$ are retained if the pH is less than 3 but are eluted if the pH is greater than about 6. Phenols, which have a $pK_a \sim 10$, do not elute unless the pH is above ~ 11. Neutral compounds that cannot be ionized, such as hydrocarbons, can be eluted with methanol or ether. Thus, we hypothesized that the organic materials in SSW could be fractionated by the scheme shown in Figure 3.

For testing this method, test mixtures containing aniline, benzoic acid, and phenol were prepared. These compounds were selected because they could easily be determined directly in aqueous solution by high pressure (or high performance) liquid chromatography (HPLC),* using an ultraviolet absorption (uv) detector. Preliminary experiments showed that with 0.1 N HCl, aniline was eluted and phenol and benzoic acid were retained. However, attempts to separate phenol and benzoic by elution with water having a pH ~ 7 failed. Separation could be achieved if the elution solvent was a pH 7 buffer. The data for a mixture of benzoic acid and phenol are summarized in Table 8. The separation of phenol and benzoic acid is excellent when a pH buffer is used. Samples of SSW from refinery A were then separated by the procedure shown in Figure 3. The same XAD column was used. (The column was regenerated by elution with methanol, then back-washed with water.) In this case, 100-ml fractions were collected. The samples were analyzed for TOC, and the results are summarized in Table 9. At this point, research on the XAD resin separation technique was stopped because the sum of the individual TOC values was more than twice the TOC measured on the SSW. This probably was due to excess methanol that had been used to prepare the column and could have been removed by more extensive washing of the column.

Separation of the organic material in SSW was also attempted using the extraction scheme shown in Figure 4. The principle of this method is that ionized organics are more soluble in water than in an organic

*The method is described in detail later in this section.

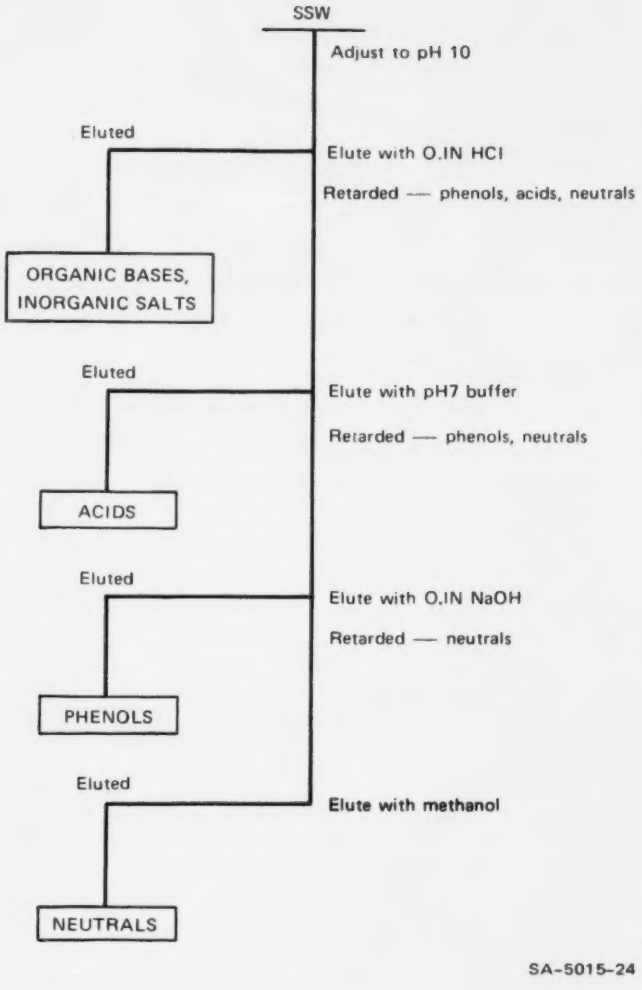

Figure 3. Separation by XAD resins.

TABLE 8. SEPARATION OF PHENOL AND BENZOIC ACID BY XAD RESINS*

Elutant	Fraction Number†	Percent Eluted‡ Phenol	Benzoic Acid
pH 7 buffer	1	0%	53%
	2	0	25
	3	0	9
	4	0	5
0.1 N NaOH	5	66	3
	6	24	3
	7	6	2
Total eluted		96%	100%

*Column contained 5 g of XAD-2 and 5 g of XAD-8, intimately mixed.

†Each fraction was 25 ml; total eluted = 175 ml.

‡A 10-ml aliquot of a solution containing 707 mg l^{-1} benzoic and 301 mg l^{-1} of phenol was eluted.

TABLE 9. TOC DATA FROM XAD RESIN SEPARATION OF STRIPPED SOUR WATER FROM REFINERIES A AND B

Fraction	A1 TOC (ppm)	B1 TOC (ppm)
Amines (0.1N HCl)	1,114	120
Acids (pH 7 buffer)	330	20
Phenols (0.1N NaOH)	900	970
Phenols (?) (50 ml H_2O)	250	50
Neutrals (75 ml methanol)	1,680	20
Total	3,374*	1,180*

*TOC values from sample prior to separation were: 1680 for refinery A and 20 for refinery B.

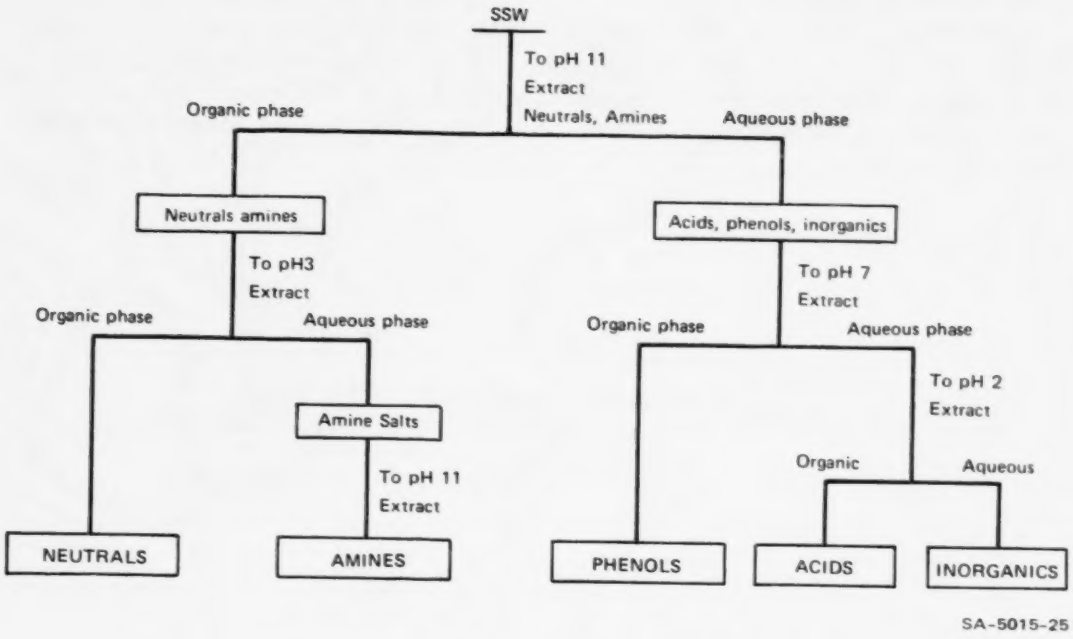

Figure 4. Separation by extraction with organic solvents.

solvent. Thus, at pH 3, amines are protonated and have a positive charge and will be more soluble in the aqueous layer. Phenols and acids are also protonated, but are not ionized and do not have a charge. Hence, they should be more soluble in the organic layer. After the sample is carried through the scheme in Figure 4, the organic layers are dried, and the solvent is removed in tared containers. The organic fraction was determined by weighing. Data obtained are reported in Table 10. A comparison of the total organic carbon values is also included in the table. The total organic material extracted shows that, with the exception of sample A1, the recoveries were poor. Some of the extracts were subjected to analysis by gas chromatography/mass spectroscopy (GC/MS) (see a following section for details). In all cases, the acid extracts contained large quantities of phenol, cresols, and xylenols, suggesting that the methylene chloride did not extract all of the phenols at pH 7. The data also suggest that methylene chloride was probably a poor solvent choice compared to ether, but we did not have the time or funds to repeat the extractions.

TABLE 10. ORGANIC CONTENT BY EXTRACTION

	Weight of Organic Materials from Refinery: (ppm)				
Sample	A1*	A2†	A3†	D1†	F1†
Neutrals and organic bases (pH 11)	313	150	337	22	57
Phenols (pH 7)	239	77	154	8	17
Acids (pH 2)	902	95	131	8	10
Total extracted	1,454	322	622	38	84
Total organic carbon	1,680	2,960		560	500

*Solvent was ether.

†Solvent was methylene chloride.

These results, coupled with the GC/MS results, suggest that the problem of separating the large concentration of phenols from the acids deserves additional research. The preliminary studies with XAD resins indicate that these resins could be used to accomplish the desired separation. Also, the separations are much sharper than we were able to achieve with solvent extraction. In retrospect, the decision to stop using them was probably an error, and it is now our opinion that the XAD resin technique could be developed into a simple, rapid, and useful technique. The major problem was that the TOC values measured in the eluted fractions were high compared to the total TOC in the samples. Several publications suggested that extensive cleanup by first washing with methanol and then large volumes of water would eliminate the background TOC. Also, the separations could be improved by adjusting the elution volume and rate.

It would also be possible to use preparative reverse-phase HPLC to separate the organic acids from the other components of SSW. The procedure for separation and analysis of phenols, which is discussed in the next section, demonstrated that aliphatic acids and benzoic acid were eluted well before phenol. We cannot make an obvious choice between XAD and reverse phase HPLC at this time, but both clearly deserve further study.

Determination of Phenolic Compounds

We have developed a simple, straightforward analytical procedure that can be used to determine quantitatively the concentration of phenol and cresols in ppm quantities in SSWs. It should be possible to generalize this method to other aqueous samples and to higher phenolics such as xylenols and naphenols. The method is based on HPLC using a reverse phase column.

The reverse phase column consists of a fine particulate silicate support to which a hydrocarbon has been chemically bonded. In this case, we used a Du Pont ODS column, which is a straight chain C_{18} alcohol bonded to the support (Waters, Spectro-Physics, and others supply similar columns that would work just as well.) The column sorbs both nonpolar and polar materials. The eluting solvent is generally an aqueous solution of a polar organic solvent that is miscible with water, such as methanol or acetonitrile. Polar compounds are eluted readily when the solvent contains a large proportion of water; nonpolar materials required higher concentration of the organic solvent. For instance, phenols are readily eluted in 1:1 methanol: water, but aromatic hydrocarbons are strongly sorbed and are eluted with about 9:1 methanol: water.

This general procedure has been further refined, using the method of "Paired-Ion Chromatography" (Waters Associates, 1975), which, in this case, involves the addition of tetrabutylammonium phosphate to the HPLC solvent system. The tetrabutylammonium salt saturates the HPLC column. The anions of acidic materials are further retained by the column. We used this technique to retain the aromatic and aliphatic acids on the column and to separate them from the other polar material that may be present in the SSW. Other experiments suggest that it may not be necessary to add the tetrabutylammonium salt to analyze for phenolics, but that it is required to analyze for aromatic acids.

Chromatograms for all the samples are given in Appendix F. The chromatograms for refineries A, D, E, and F show a substantial number of peaks which are eluted before phenol. These peaks were not positively identified but comparison with chromatograms of benzoic acid (see Figure F-1) suggest that they are organic acids. Additional work with different solvent mixtures would be required to resolve these peaks.

Analysis of SSW Extracts by GC/MS

Samples of SSW from Refineries D1 and F1 were adjusted to pH 11, pH 7, and then pH 2 and were extracted three times at each pH with methylene chloride. The extracts were analyzed by GC/MS. The results are summarized in Table 11.

No organic acids or bases containing nitrogen were observed. We did not attempt to show that aliphatic and aromatic acids could have been observed if they were present. The main conclusion is that the separation of phenolics by extraction is very poor, since phenol and cresols were found in the extracts at all three pH levels. The data also confirmed our suspicions, based on the HPLC analyses, the xylenols and trimethyl phenols were also present. Quantitative data were not obtained.

Characterization of Organics by Gel Permeation Chromatography

Gel permeation chromatography (GPC) is a method for determining the molecular size distribution of complex organic mixtures. The GPC traces shown in Figure 5 were obtained on Waters Porasil Ax and Cx columns in series, using 100% water as the eluting solvent, and a 254-nm uv detector, which will detect aromatic compounds. This column combination gives good separations over the equivalent molecular weight range of about 50 to 500. The data confirmed that the major aromatic constituents were phenolics. The peaks in the range of about 80 to 120 correspond to phenol and cresols; the peaks at about 120 correspond to dimethyl phenols.

TABLE 11. SEMIQUANTITATIVE ANALYSIS OF SSW EXTRACTS BY GC/MS (ppm)

Compounds Identified	Refinery D1			Refinery F1		
	pH 11	pH 7	pH 2	pH 11	pH 7	pH 2
C_3H_7-Benzene*	~5†	--	--	--	--	--
Aniline or Methyl pyridine	~30†	--	--	--	--	--
Phenol	60	270	100	80	120	90
o-Cresol	30	30	3	3	2	--
p-Cresol	90	200	30	30	30	3
Xylenol (3 isomers)	~100†	~5†	~1†	~1†	--	--
Trimethyl phenols	~10†	--	--	--	--	--

*Isopropyl benzene or trimethyl benzene or methyl ethyl benzene. Positive identification was not attempted.

†Very rough estimates; quantitative measurement was not attempted.

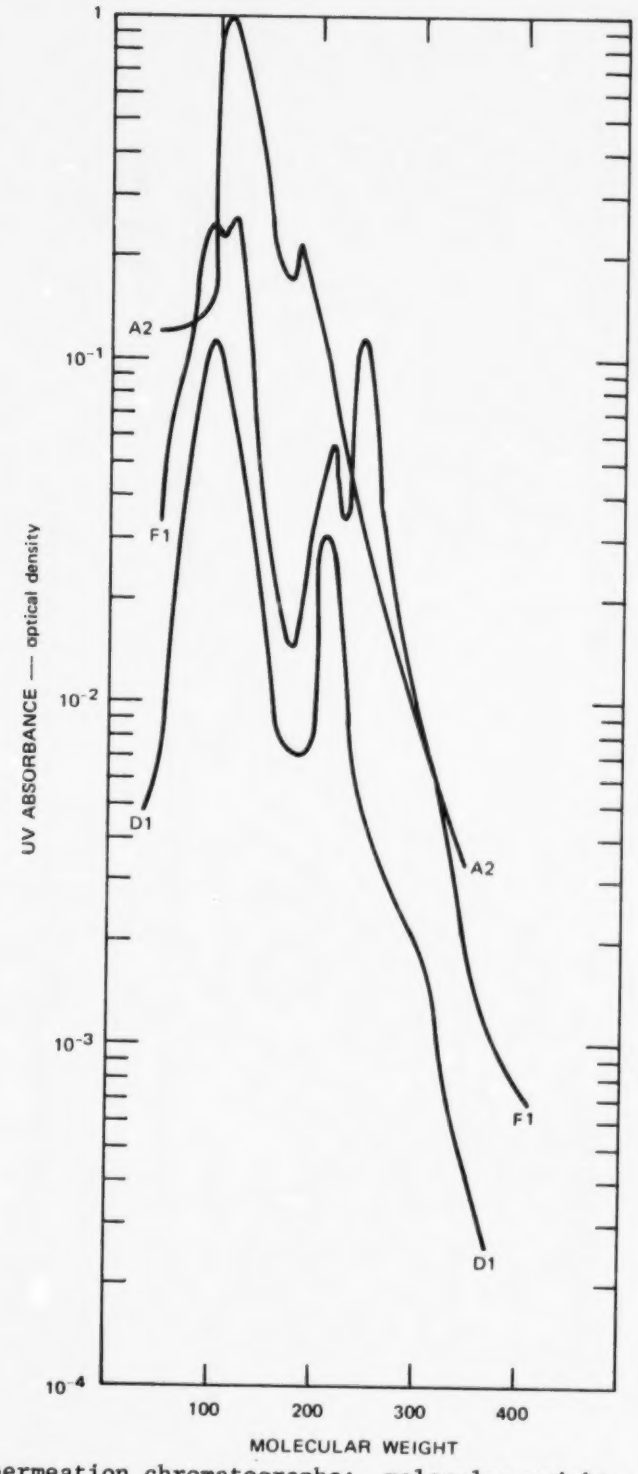

Figure 5. Gel permeation chromatographs: molecular weight as a function of UV absorbance on Porasil Ax and Cx columns. Mobile phase: 100% H_2O.

The peaks in D1 and F1 at 200 and 250 were not identified. The significant result of these experiments is that the amount of high molecular weight aromatic compounds (molecular weight above 300) in the SSW is very low.

The results of our analysis for total organic carbon, phenols, and weak acids are given in Table 12. The data show that roughly 12 to 40% of the organic material can be accounted for as phenol and cresols. We also observed xylenols in small quantities in many of the samples but no attempt was made to quantify these compounds. Specific carboxylic acids were not identified, and their presence can only be inferred from the potentiometric titrations. Data for weak inorganic acids (HSCN and H_2SO_3) from Table 5 were used to calculate concentrations for weak organic acids from the total weak acid concentrations derived from the potentiometric titrations. Organic acids account for the majority of the total weak acids for sour waters from refineries that contain measurable amounts of weak acid.

TABLE 12. ANALYSIS FOR TOTAL ORGANIC CARBON, PHENOLS, AND WEAK ACIDS (ppm)

Analysis	Refinery A1	A2	A3	B1	C1	D1	E1	F1	G1	H1
TOC--ppm	1680	2960	ND	20	260	560	240	500	160	ND
Loss on ignition	ND	2186	ND	100	589	313	393	276	71	ND
Potentiometric titrations										
Total weak acid* (meq/ℓ)	36.0 ± 0.5†	ND	39.3 ± 0.5†	ND	<2.0†	2.9 ± 0.5†	<2.0‡	4.3 ± 0.5†	<2.0‡	<2.0‡
Organic weak acid (meq/ℓ)§	ND	--	ND	--	<0.1	2.1 ± 0.5	<0.3	3.0 ± 0.5	<2.0	<2.0
Direct determinations by liquid chromatography										
Phenol	ND	375	ND	4	62	202	44	182	48	269
m- and p-Cresol	ND	56	ND	3	23	122	14	21	20	31
o-Cresol	ND	35	ND	3	9	75	13	12	17	8
Total	--	466	--	10	94	299	71	215	85	308
Percent of TOC accounted for by phenols	--	12	--	38	27	40	23	33	40	--

ND = Not determined.

*Includes weak organic acids and the weak inorganic acids HCNS and H_2SO_3. Will also include H_2S when present.

†Titration run on sample as is. Since samples were generally basic, this titration will show H_2S.

‡Titrations run on samples pretreated with acid. Much of the hydrogen sulfide would have volatilized during pretreatment. The results probably do not include any sulfides.

§Calculated from total weak acids and the data in Table 5 for SCN-S and SO_2-S which were converted to meq/ℓ by using factors of 32 mg S = 1 meq SO_2-S and 32 mg S = 1 meq SCN-S.

SECTION 7

CAUSES FOR AMMONIA FIXATION

Organic acids, sulfur acids, heavy metals, and measurement interferences have been postulated as causes of ammonia fixation (see Section IV). Analysis of the refineries' sour water samples indicates that heavy metals are probably not involved since heavy metal concentrations were low. Measurement interferences are not a major factor except when low effluent concentrations are required. Evidence points to weak acids, such as HSCN, and organic acids ($pk_a < 6$), as the primary cause of ammonia fixation. In some sour waters, strong sulfur acids such as sulfuric and thiosulfuric acid may be involved. These acids are the result of oxidation of sulfides in the refinery sour water system.

Tables 13 and 14 contain the evidence for these conclusions. Table 13 contains data from analysis of six refinery samples. Table 13 was prepared from data in Table 5 and Table 12. Refinery A was excluded from the table because caustic addition is used in that refinery to increase ammonia removal. Refinery E was excluded because, as a matter of design, it does not incorporate removal of all the ammonia from the sour water. Table 13 shows that the residual ammonia level is high when the acid level is high and low when the acid level is low. The same data are shown in Figure 6. In the figure, a 45^{o} line has been drawn to indicate the results that would be expected if residual ammonia equivalents were equal to acid equivalents. All of the refineries should fall close to this line if they are stripping hard enough to remove all but fixed ammonia. Some of the refineries fall above the line, which we interpret to mean that they are not stripping hard enough. In general, however, there is a good correspondence between acid level and residual ammonia.

Table 14 contains data generated in our laboratory from samples of unstripped sour water. With these samples, chemical analysis was not used to determine acid concentrations. Total acid content was determined by batch stripping to a bottoms pH of 6 (Dobrzanski, 1974). This method assumes that acids are the only cause of ammonia fixation. Physical-chemical calculations of pH versus concentration of weak acid ($pK_a = 4.8$) and ammonia nitrogen show that when the molar concentration of the two are equal, the pH will be near or slightly below 6. Any strong acid present will contribute its own equivalent of ammonia to the residual measured at pH 6. The only confusion introduced by a strong acid is that it lowers the pH of the true equivalence point. This means that at pH 6 we can determine only the approximate amount of strong and weak acid present by measuring the ammonia level.

TABLE 13. ACID AND AMMONIA RESIDUALS
IN REFINERY STRIPPED SOUR WATERS

Refinery	Weak Acid* (meq/ℓ)	Weak Acid* (pK_a)	Strong Acid† (meq/ℓ)	Total Acid (meq/ℓ)	Ammonia Residual (meq/ℓ)
B	< 2	--	--	2.0	1.0
C	< 2	--	2.4	4.4	11.0
D	2.9 ± 0.5	4.9	0.5	3.4	2.1
F	3.9 ± 0.5	5.0	1.0	4.9	6.2
G	< 2	--	0.0	2.0	2.1
H	< 2	--	3.4‡	5.4	4.2

*Determined by potentiometric titration. This includes HSCN, H_2SO_3, and organic acids.

†Thiosulfuric and sulfuric acid. Sulfuric acid is not present in significant amounts so this represents $S_2O_3^{=}$.

‡Estimated by sulfur balance.

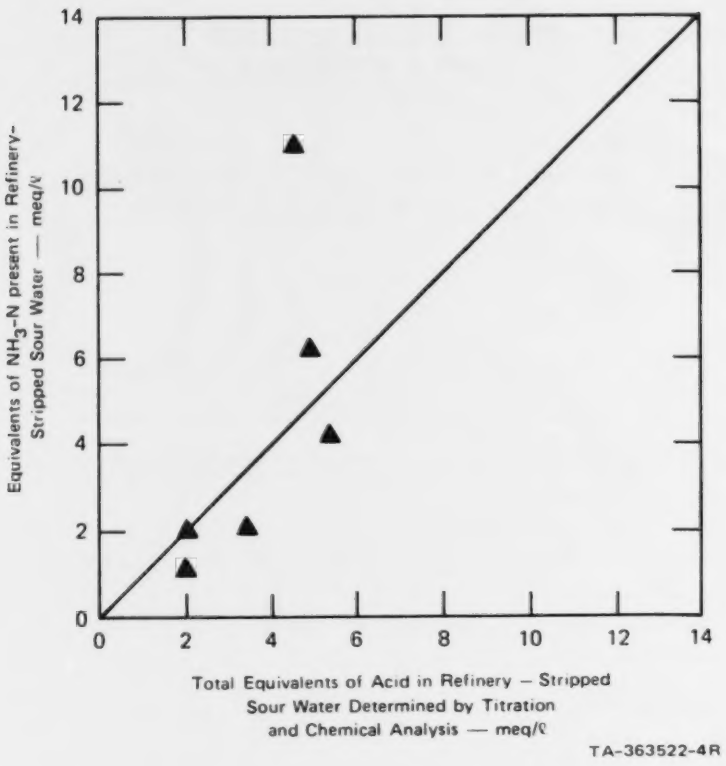

Figure 6. Correlation of ammonia residual with acid content of sour water.

TABLE 14. ACID AND AMMONIA RESIDUALS IN LABORATORY STRIPPED SOUR WATERS

Refinery	Ammonia* Residual (meq/ℓ)	Total Acid† (meq/ℓ)	Titrated‡ Weak Acid (meq/ℓ)
A	57.0	45.7	39.3
C	3.3	3.6	ND
D	3.14	3.6	ND
F	1.3	1.4	ND

ND = not determined.

*Determined in a laboratory column with 8 equilibrium stages and total steam rates in excess of 1.3 lb/gal. This would give better than 99% removal of ammonia if no fixation occurred.

†Determined by batch stripping with nitrogen and steam to a bottoms pH of 6.

‡Potentiometric titration. The pK_a was 4.8.

The ammonia residual measurements shown in Table 14 were made on samples of the same sour water after it had been severely stripped in our laboratory stripping column. For three of the refinery samples, Table 14 shows a close correspondence between the estimated acid content and the ammonia residual after severe stripping. Only sample A3, with a high ammonia residual, does not fit the pattern closely. For refinery A, the ammonia residual exceeds the estimated total acid by a significant amount. There are two probable explanations for this disagreement. First, because refinery A contains strong acids, the total acid estimated, which is made at pH 6, will be an underestimate of the true total acid content since the true equivalence point will be below pH = 4.8. Second, and probably the more important reason, refinery A contains significant amounts of organic nitrogen compounds, which means that the ammonia concentration measured after stripping in the laboratory column will be an overestimate of the fixed ammonia level.

Analyses of stripped sour waters from refinery A have shown that the organic nitrogen compounds in this sour water hydrolyze to ammonia during the distillation at pH 9.5, which is part of the ammonia measurement procedure. At the temperatures in a stripping column, these hydrolysis reactions occur rapidly if conditions are strongly acidic or basic, but quite slowly when the pH is 6-8. Regardless of pH, the reactions occur very slowly at room temperature. During stripping the laboratory column, the sour water is hot and is between a pH of 6-8 for about 10 minutes, and significant hydrolysis would not occur. However, when the bottoms from the column are distilled to measure ammonia, they would be hot and at pH 9.5 for 10 minutes. Here, significant hydrolysis could occur, and the ammonia measurement could be a significant over-estimate of the true ammonia level.

During the batch stripping test to estimate total acid, the sour water is hot and is at pH 6-8 for over an hour. Because of the long residence time, significant hydrolysis could occur and the ammonia generated by the hydrolysis would be stripped out. When the bottoms from this batch stripping are distilled at pH 9.5 in preparation for an ammonia measurement, there would be little unhydrolyzed organic nitrogen left, and the ammonia concentration measured would be close to the true value. When the measured ammonia level in the bottoms from the batch stripping is converted to acid equivalents, it would be a close estimate of the true acid concentration. No estimate of strong acid concentration based on chemical analysis of this sample is available to calculate the correct total acid concentration from the sum of titrated weak acid plus strong acid, but if it were available, we would expect the two estimates to agree closely.

A few experimental stripping runs were conducted to confirm the ammonia fixation potential of a weak organic acid and sulfur acids. Sulfur acids were created by allowing ammonium sulfide solutions to sit exposed to air for several hours. Benzoic acid (pK_a = 4.2) was used as the weak acid.

Table 15 shows the results of stripping freshly prepared ammonium sulfide solutions with benzoic acid added. Since these solutions were prepared from deaerated water, ammonium hydroxide, and H_2S gas, we feel certain that few sulfur oxidation products were present. At high steam rates without benzoic acid, both ammonia and sulfide removal is practically 100%. This means that any change in removal efficiency will be due to chemical effects alone. At the same high steam rate, addition of 100 ppm of benzoic acid (0.82 meq/ℓ), which is equivalent to 11.5 ppm NH_3-N, causes the bottoms pH to drop and the ammonia nitrogen concentration to rise 9.4 ppm (11.5 ppm expected); 500 ppm of benzoic acid causes a concentration increase of 54.4 (57.5 ppm expected). Since these concentration measurements are only precise to ±5%, this experiment gives convincing evidence that a weak acid will fix an equivalent amount of ammonia. The weak acid causes ammonia fixation by causing the bottoms pH to fall to the point where ammonia is not volatile. The same effect seems to be evident at low steam rates. At low steam rates, however, bottoms ammonia levels reflect both fixation and insufficient steam to strip unfixed ammonia. The fact that both effects are present is seen in the bottoms pH, which is basic rather than approximately neutral, as in the case with high steam rates. The pH in the bottoms tends to be lower when benxoic acid is present, however, and the ammonia level tends to be higher. Apparently, at the low steam rate even the change in ammonia volatility caused by small changes in pH is sufficient to raise bottoms ammonia levels by about the equivalent of the acid present.

Table 16 shows the results of two artificial feeds that were allowed to oxidize. The steam rates used were sufficient to strip all ammonia that was not fixed. The run without benzoic acid shows 25 ppm fixed ammonia due to the effects of oxidation. Benzoic acid addition causes an additional amount of ammonia to be fixed.

Figure 7 summarizes these results.

SOURCES OF ACIDS THAT CAUSE AMMONIA FIXATION

The operations of the eight refineries sampled in this program were examined to determine if there was any relationship between crude type or refinery processes and the acid levels in the refinery sour

TABLE 15. H_2S AND NH_3 STRIPPING TESTS USING FRESH ARTIFICIAL FEED

	Run Number						
	813-2	819-2	819-1	827-1	824-1	824-2	827-2
Steam rate*							
Stripping steam (lb/gal fresh feed)	1.05	1.21	1.13	0.92	0.38	0.29	0.31
Total steam	1.46			1.32			0.67
Feed							
H_2S (ppm)	2000†	1617	1617	1843	1436	1397	1552
NH_3-N (ppm)	1100†	700	650	690	720	700	660
Benzoic acid (ppm)	0	0	100	500	0	100	500
pH	7.9	7.3	7.3	7.5	8.0	8.0	7.8
Bottoms							
H_2S (ppm)	< 0.1†	< 0.1	< 0.1	< 0.1	2.2	0.5	0.2
NH_3-N (ppm)	7†	1.6	11	56	37	56	78
pH	7.8	8.1	7.1	7.5	9.3	9.3	8.9
NH_3 Efficiency (%)	99	100	98	92	95	92	88
H_2S Efficiency (%)	100	100	100	100	100	100	100
Temperatures (°F)							
Reflux	185	205	212	190	161	160	157
Feed	150	175	170	170	162	163	175

*Stripping steam is the amount of steam leaving the feed tray. Total steam is the steam fed to the column minus the steam equivalent of column heat losses.

†Tests using Hach colorimetric procedures for these measurements only.

TABLE 16. H_2S AND NH_3 STRIPPING TESTS USING OLD ARTIFICIAL FEED

	Run Number	
	818-4	819-3
Steam Rate*		
Total steam (lb/gal)	1.44	1.89
Stripping steam (lb/gal)	1.27	1.18
Feed		
H_2S (ppm)	2000†	1229
NH_3-N (ppm)	660	680
Benzoic acid (ppm)	0	100
pH	7.9	7.9
Bottoms		
H_2S (ppm)	< 0.1†	< 0.1
NH_3-N (ppm)	25	37
pH	7.4	6.8
NH_3 efficiency (%)	96	94
H_2S efficiency (%)	100	100
Overhead Temperature (^oF)	200	200
Feed Temperature (^oF)	164	170

Note: **All NH_3 measurements are by ion specific** electrode. 100 mg/l benzoic acid is equivalent to 11.5 mg/l NH_3-N.

*Stripping steam is the steam leaving the feed tray. Total steam is the steam fed to the column minus the steam equivalent top column heat losses.

†Hach kit - Alka Seltzer Test. All other sulfides by methylene blue.

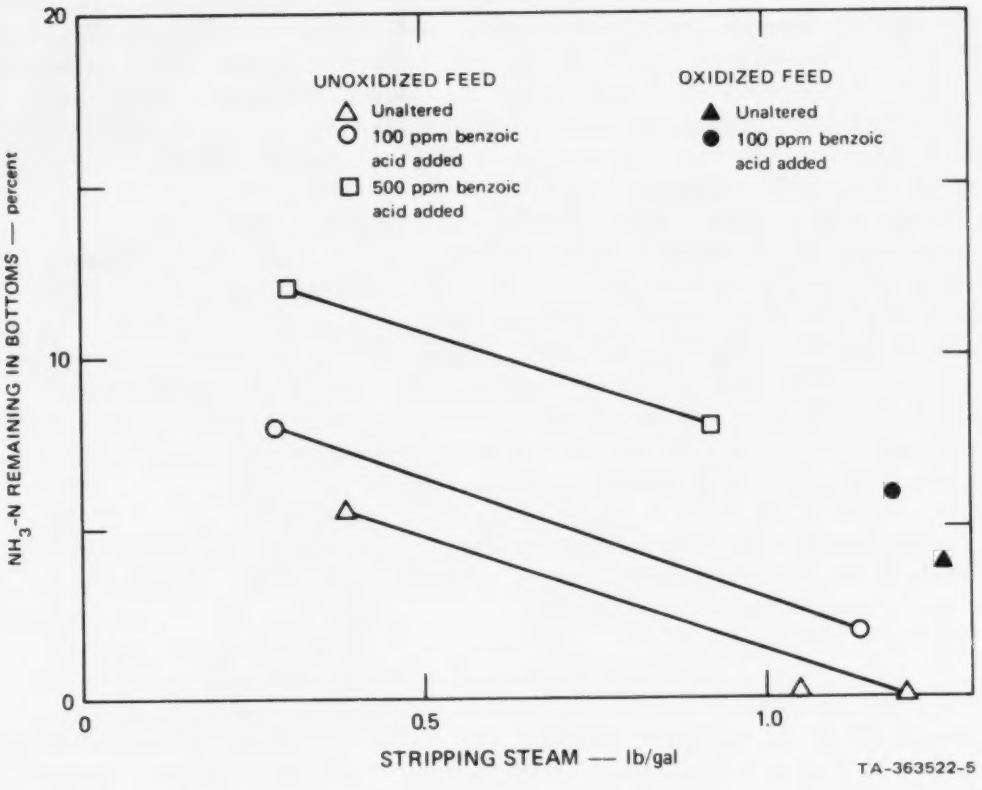

Figure 7. Effect of benzoic acid and feed oxidation on ammonia removal from sour waters.

water. Table 17 summarizes the results of this study for the 6 refineries which provided the most complete operational data. More detailed data is included in Appendix G. The refinery processes which contribute more than 10% of the sour water to the stripper sampled have been identified for each refinery. The major crude processed during the study period is identified. The acid levels shown in Table 5 and 12 have been collected and repeated on the Table to clarify the discussion.

The data in Table 17 do not show a clear pattern. There is no clear relationship between the weak inorganic and strong sulfur acid levels and the refinery processes contributing sour waters. The practice of adding polysulfides to inhibit corrosion in the sour water system does not correlate with sulfur containing acids. There does appear to be some association between organic acid levels and crude processed. The two refineries, A and D, which show significant amounts of weak organic acids both are processing crude slates where California crude oils predominate. It may also be significant that both refineries have cokers, but any association of weak acids with cokers and California crudes must be considered tentative. The fact that refinery C processes California crude, and has a coker, but does not have high organic acid levels in its sour water weakens any association of organic acids in sour water with cokers and California crudes. In addition, Refinery A, which has a significantly higher level of organic acids than the other refineries is the only refinery with a gas oil vacuum still as a source of sour water.

Additional refinery sour waters would need to be sampled in order to determine the association between organic acid levels and refinery processing or crude slates. It may be necessary to identify the cokers used as to type (i.e., fluid or delayed). The additional refineries sampled would have to include several with the configuration of Refinery A but processing different crude slates. It would be important also to choose refineries to introduce more variation in sour water acid levels. Finally, it would be most helpful to analyze sour wastes produced by individual process units rather than only the composite sour water.

There are two reasons why the sample of refineries chosen for this study is not adequate for identifying the sources of the acids which cause ammonia fixation. First, most of the refineries sampled produce sour water with total acid levels in the range of 3-5 meq/ℓ. Therefore, even though each refinery has a different processing scheme, they are almost identical in terms of sour water acid level. Secondly, the sample is probably too small to develop a good correlation.

TABLE 17. SOUR WATER ACID LEVELS AND REFINERY PROCESSES FEEDING SOUR WATER SYSTEM

Refinery	Crude: California	Crude: Texas	Crude: Foreign	Refinery Processes: Polysulfide for Corrosion Control	Refinery Processes: Hydrocracker	Refinery Processes: Cat Cracker	Refinery Processes: Coker	Refinery Processes: Hydrotreater	Refinery Processes: Reformer	Refinery Processes: Crude still	Refinery Processes: Gas oil vacuum still	Sour Water Acid Levels (meq/ℓ): Weak Organic Acid	Weak Sulfur Acids	Strong Sulfur Acid	Total Acid
A	X						X		X	X		36	0	2.8	38.8
B	X				X							<2	0	0	<2
C	X			X	X	X	X	X	X			<0.1	1.9	2.4	4.3 - 4.4
D	X					X	X		X			2.1	0.8	0.5	3.4
E			X			X	X		X			<0.3	1.7	3.4	5.1 - 5.4
H		X				X	X					<2	<0.1	3.4	3.4 - 5.4

SECTION 8

EXPERIMENTAL APPARATUS FOR BENCH-SCALE STRIPPING OF SOUR WATERS

Figure 8 is a schematic of the bench-scale stripping apparatus that was used for the experimental program. Its key features are:

- Two 5-plate 1" I.D. Oldershaw columns to provide for 5- and 10-plate experiments as well as mid-column caustic injection.
- A special reflux measuring trap at the bottom of the two Oldershaw columns to permit measuring liquid flow rates in the column.
- A distillation head that provides no more than one equilibrium stage and at the same time allows direct return of the reflux stream to the column top.
- A heater for the vapor path from the still top to the condenser so as to eliminate premature condensation.
- Caustic injection ports at the top, middle, and bottom of the column.
- A temperature control for the condenser which permits reproducible control of the overhead condensate temperature.
- A still pot (and heater) with a constant level feature so that bottoms collection is automatic. The still pot will have low holdup to speed system response to changes in operating variables.
- A special column feed section that permits measurement of temperature on the feed tray.
- A low speed peristaltic feed pump.
- A temperature-controlled feed preheater.
- An overhead gas condenser to collect any water leaving the column with the stripped ammonia and sulfide.
- An overhead gas scrubber to eliminate dangerous emissions of hydrogen sulfide.

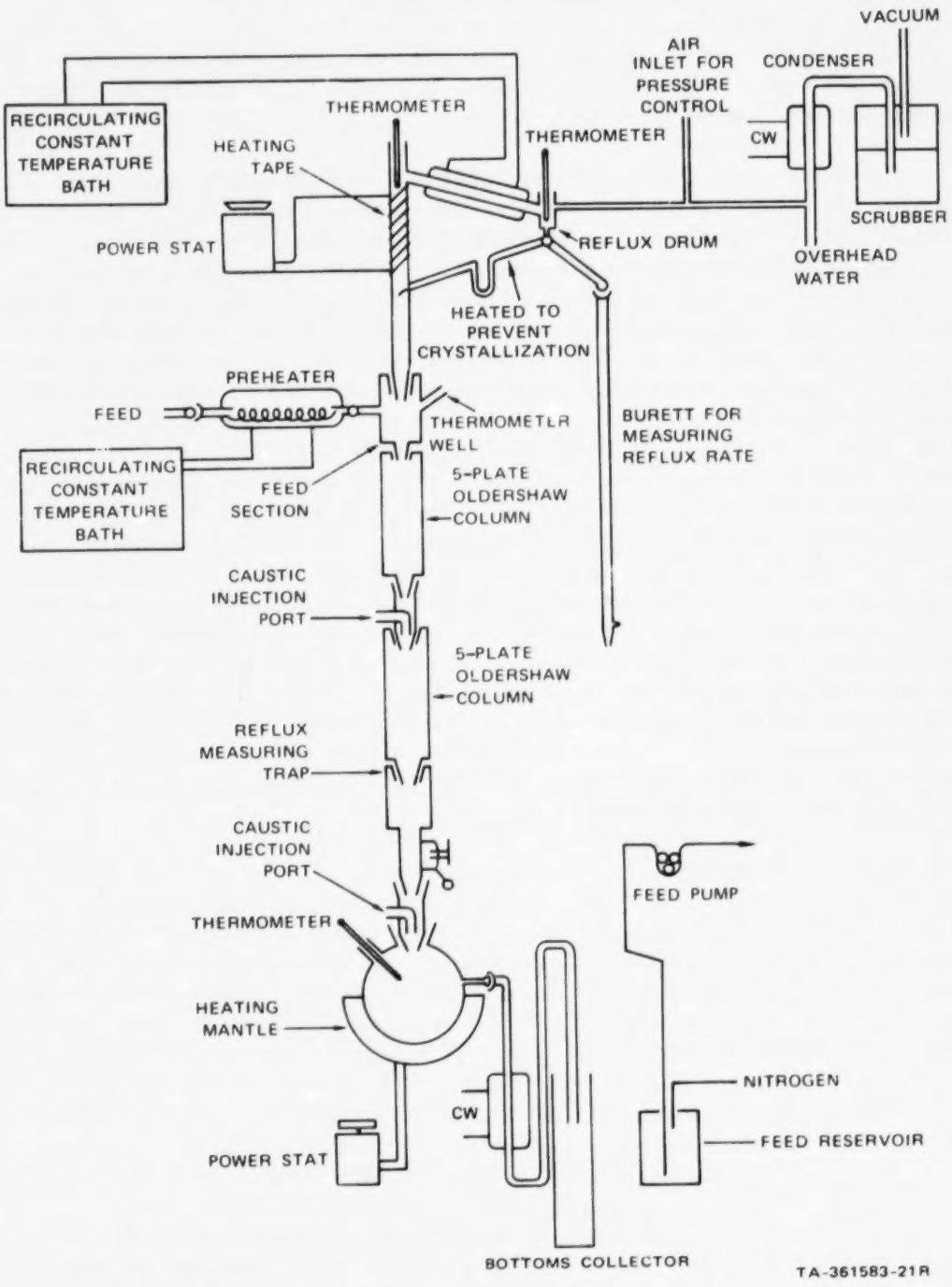

Figure 8. Schematic of bench scale sour water stripper.

Figure 9 is a photograph of the stripper.

All water rates in and out of the column can be measured. Except for the mass represented by the sulfide and ammonia, complete material balances can be calculated.

The fresh feed rate can be accurately determined by a volume difference measured over the duration of an experimental run. The bottoms rate can be determined in the same way. Column heat loss and total heat rate can be determined by using the special reflux trap included in the column bottom. Column heat loss is measured first by adjusting the steam rate to achieve steady-state operation at the point just before a reflux stream forms. The liquid rate measured in the trap is the steam equivalent of the column heat loss. Heat loss can be measured once and considered constant for each experimental setup. For the setup used it was 1.2 g steam/min. Column heating rates can be measured by operating the column without feed (at steam rates sufficient to provide reflux) and measuring the liquid flows in the special trap. For these measurements, the overhead condenser is operated at 20°C to provide complete condensation. A series of steam rate determinations were used to develop a calibration curve for the powerstat that controls the bottom heater, so that during the experimental program column heating rate could be determined approximately from the powerstat setting. For some runs the column heating rate was measured to confirm the calibration curve. These confirmation runs showed that the heating rate could not be determined accurately from the calibration curve. Therefore, for all experimental runs the column heating rate was determined by a mass and heat balance around the column top using feed rate and reflux rate.

Reflux rate was measured during a run by diverting the flow from the reflux drum into a burett. These diversions were made early in a run so that they would not affect the concentration measured in the bottoms at the end of a run. Diversion of the reflux stream does upset the heat flow in the column and would interfere with accurate measurement of the reflux rate. The maximum error is about 10% and does not interfere significantly with interpretation of the stripping results. Steam flow in the column below the feed tray was calculated from the reflux rate by using heat balances around the feed tray. These calculations neglected the heat of vaporization of the ammonia and sulfide present, but the error does not significantly interfere with interpretation of the results.

The column was operated with liquid rates of from 7 to 20 cc/min. With these flows, plate efficiency in the same size Oldershaw column was found by experiment to be 50%-60% (Collins, 1946). A flow of 20 cc/min was preferred to lower flows, but some feeds foamed badly unless liquid rates were low.

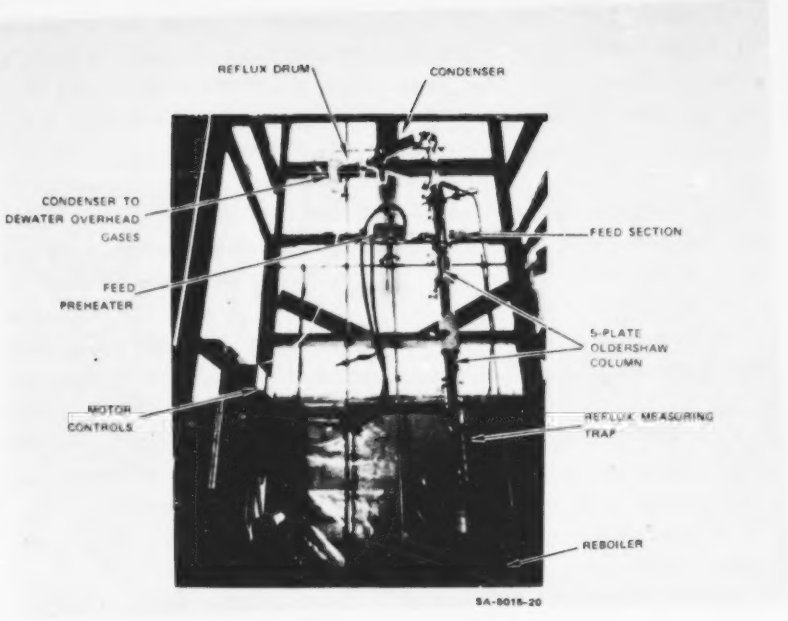

Figure 9. Bench-scale sour water stripper.

SECTION 9

CAUSTIC ADDITION TO FREE FIXED AMMONIA

Three refinery sour waters were chosen for laboratory stripping tests to determine the effectiveness of caustic addition for freeing fixed ammonia. Refinery A water was chosen because it was known to have a high ammonia residual. The refinery routinely adds caustic to the stripper. Water from Refinery C was chosen because it could be characterized as relatively low in dissolved organic carbon levels but highly oxidized, as indicated by the high free sulfur concentration. Refinery F water was chosen because it was not highly oxidized but had a relatively high concentration of dissolved organic carbon.

Table 18 summarizes the characteristics of the feeds and shows the results of the two methods used to predict fixed ammonia levels. These methods were weak acid titration of stripped sour water and batch stripping of the raw feed. Also shown in the table are the results of bench scale continuous stripping runs without caustic addition. For samples C and F the agreement between observed and predicted fixed ammonia is very good given that all of the estimates were not made using the same sample. The disagreement shown by Refinery A is expected, since this refinery's sour water contains hydrolyzable nitrogen compounds. These hydrolyzable nitrogen compounds are not detected in the titration or batch strip prediction of fixed ammonia. Because of short residence times in the laboratory stripping column, these nitrogen compounds will contribute an apparent fixed ammonia to the laboratory stripped samples from Refinery A when caustic is not added to control pH. Table 18 shows that the feed from Refinery A contains approximately 200 ppm of apparent fixed ammonia. High steam rates (~1 lb/gal stripping steam or ~1.4 lb/gal total steam) were used in a column with approximately eight equilibirum stages, (ten Oldershaw plates plus reboiler and reflux drum). These conditions are probably severe enough to strip all but fixed ammonia.

Single-Point Caustic Addition Studies

The results of the batch stripping tests were used to determine the amount of fixed ammonia in each feed. These determinations would exclude apparent fixed ammonia due to hydrolyzable nitrogen compounds. The ammonia concentrations were converted into milliequivalents per liter (meq/ℓ) of sodium hydroxide. This sodium hydroxide concentration

TABLE 18. COMPOSITION OF SOUR WATERS USED IN STUDIES OF CAUSTIC ADDITION TO FREE FIXED AMMONIA (ppm)

Refinery	H_2S	NH_3-N	pH	Predicted Fixed Ammonia-N: Weak Acid Titration Plus Strong Acids	Predicted Fixed Ammonia-N: Batch Strip	Predicted Fixed Ammonia-N: Fixed Ammonia-N in Laboratory Stripping
A3	3172	3264	8.7	540*	640	840
C2	3362	1942	8.7	95†	50	46
F2	2954	2338	9.4	68†	20	17

*Potentiometric titration of sample A3 stripped in our laboratory to measure weak acids, but strong acids were estimated from analysis of sample A1, which was stripped by the refinery.

†Estimated from analysis of samples C1 and F1.

was defined as the stoichiometric caustic dose. This stoichiometric dose does not include any caustic equivalent to the apparent fixed ammonia. A series of stripping runs for each feed was made in the ten-plate Oldershaw column at ~1 lb/gal stripping steam. Caustic was added at rates that were approximately 60%, 90%, and 110% of the stoichiometric dose. The caustic was added to the feed, the middle of the column (just above Plate 5), or the reboiler. A total of nine experimental conditions were checked. Run conditions were chosen to be in random order, and some runs were duplicated to check reproducibility. The run data is shown in Appendix E.

Effects on Ammonia Residual

Figures 10, 11, and 12 show the effects of adding caustic to the three feeds. For refineries A and C, which have the higher fixed ammonia levels, the results fit into a clear pattern. Practically all of the fixed ammonia can be freed by adding the 100% stoichiometric dose to the column top. Almost all of apparent fixed ammonia is eliminated by this caustic dose. The small pH increase due to the caustic addition eliminates almost all of the unhydrolyzed nitrogen compounds in the bottoms. The pattern also indicates that for maximum ammonia removal, the proper place to introduce caustic is high in the column. For example, with feed from Refinery A, ammonia removal achievable with a 100% stoichiometric caustic dose increases from 85% to 99% as the caustic application point is moved from the column bottom to the column top. For Refinery C with a much lower fixed ammonia level, the direction of the effect is the same; it is simply not as dramatic. Refinery F, with a very low fixed ammonia level does not show a clear pattern. The reason is that for Refinery F the fixed ammonia level is so low (20 ppm) that the ammonia level measured contains a substantial variance introduced by differences in column temperatures and steam rates from run to run.

At very low caustic dose rates and at very high dose rates, the differences in effectiveness that are related to the caustic application point become smaller. Some additional experimental work at high dose rates (in excess of 120% stoichiometric) would be required to determine if column bottom addition could ever be as effective as column top addition. Extrapolation of the curves shown in Figures 10 and 11 shows that it could be, but consideration of the equilibrium staged nature of the stripping process suggests that it could not be. After enough caustic has been added to the reboiler to increase the bottoms pH to 11, no further increase in ammonia volatility is possible and the ammonia residual becomes a function only of the steam rate.

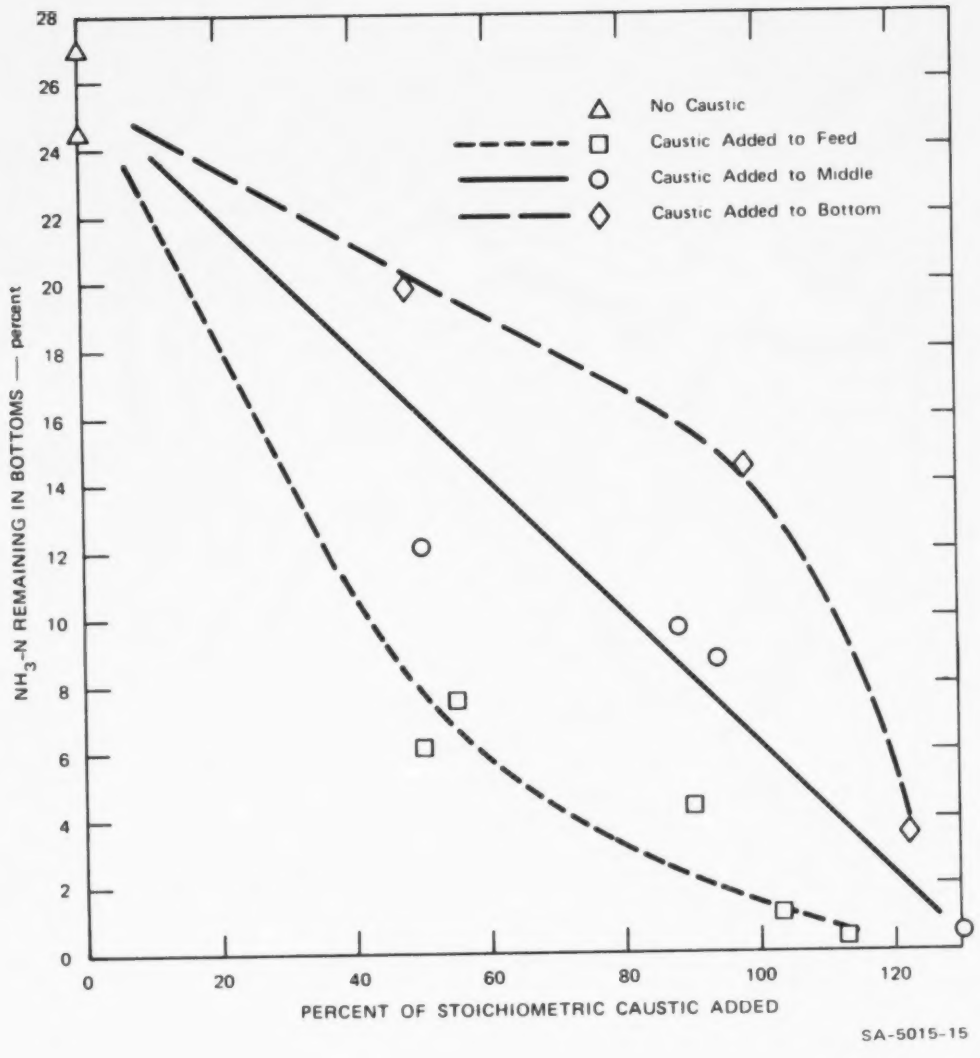

Figure 10. Refinery A: NH_3 removal efficiency at 1.03 lb/gal stripping steam (fresh feed basis) with caustic added at a single point in the column.

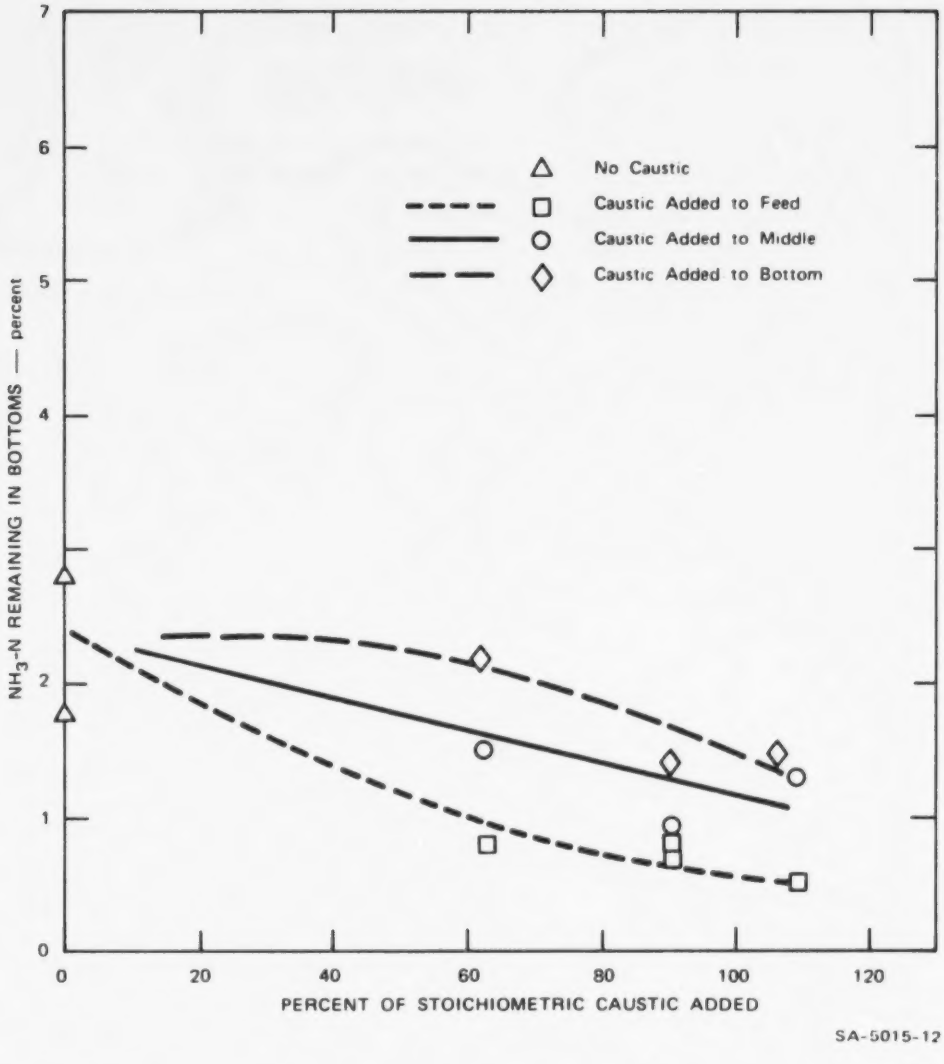

Figure 11. Refinery C: NH_3 removal efficiency at 1.04 lb/gal stripping steam (fresh feed basis) with caustic added at a single point in the column.

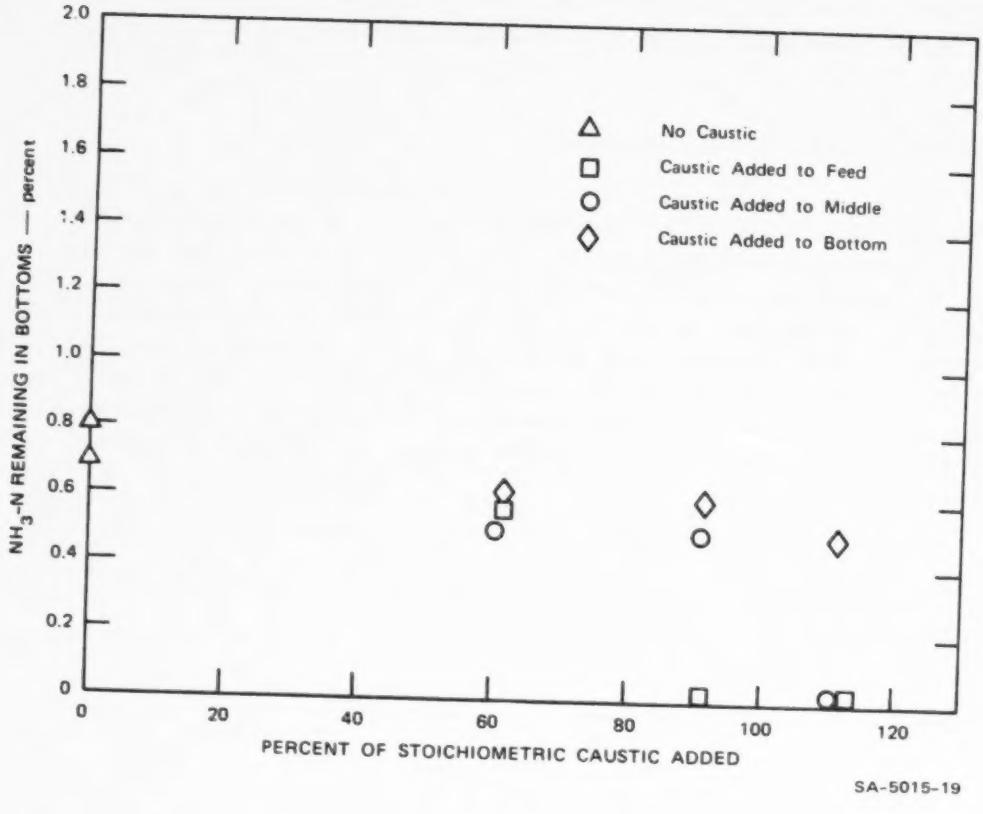

Figure 12. Refinery F: NH_3 removal efficiency at 1.04 lb/gal stripping steam (fresh feed basis) with caustic added at a single point in the column.

Effects on Sulfide Residual

Figures 13 and 14 show the effect of caustic addition on the sulfide removal efficiency achieved with feed from refineries A and F, respectively. There is no pattern to the results, which suggests that neither caustic addition rate nor application point had any effect on the individual feeds. Comparison of the two feeds shows that they yielded the same sulfide removal efficiency. This occurred despite the fact that caustic doses received by these feeds differed by a factor of 40 (i.e., 100% stoichiometric doses differed by a factor of 40).

MULTIPLE-POINT CAUSTIC INJECTION

Figure 15 shows some multiple-point caustic injection runs for Refinery A. These runs have been shown along with the estimated responses for single-point caustic injection. The results show that multiple-point injection tends to be inferior to single-point injection. For example, adding 90% of the stoichiometric dose at the feed and column middle (45% at feed and 45% at middle) yields an ammonia residual of 8% (92% removal). If it had all been added to the top, the ammonia residual would have been only 2% (98% removal). Changing caustic injection from a single point to two points had no effect on the sulfide removal efficiency.

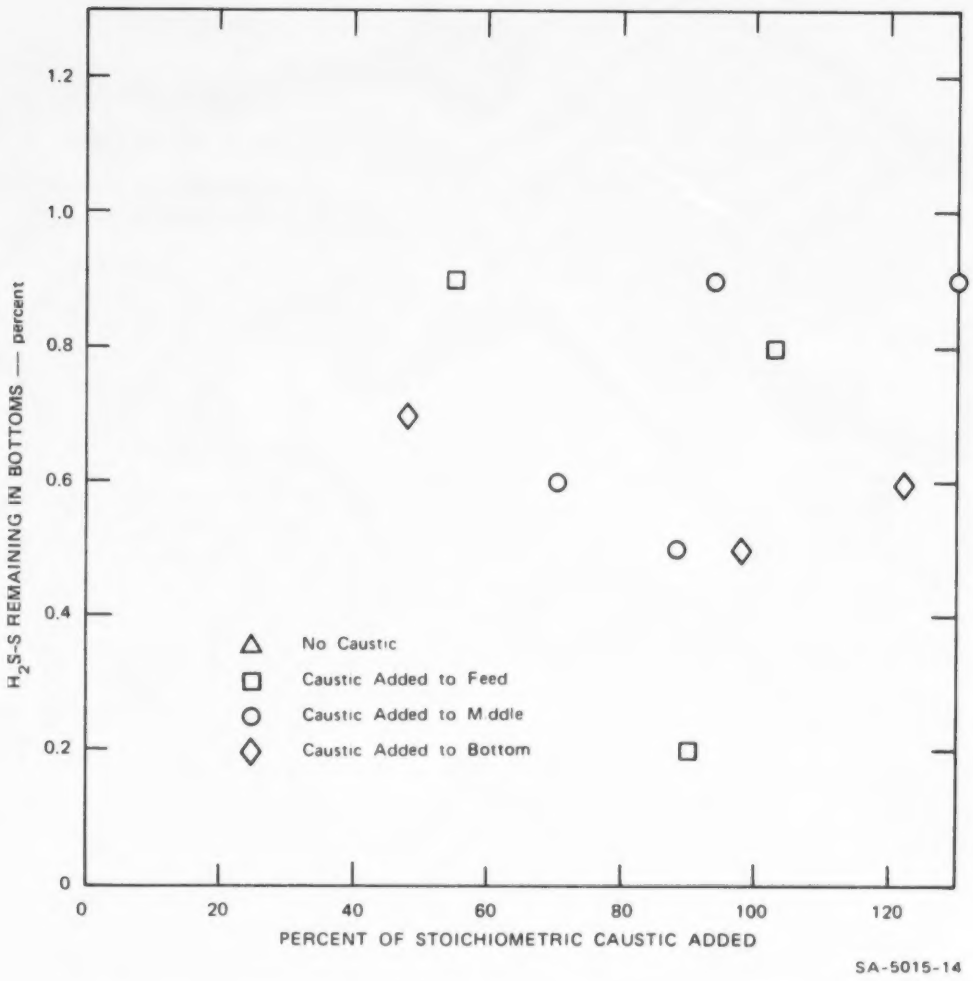

Figure 13. Refinery A: H_2S removal efficiency at 1.03 lb/gal stripping steam (fresh feed basis) with caustic added at a single point in the column.

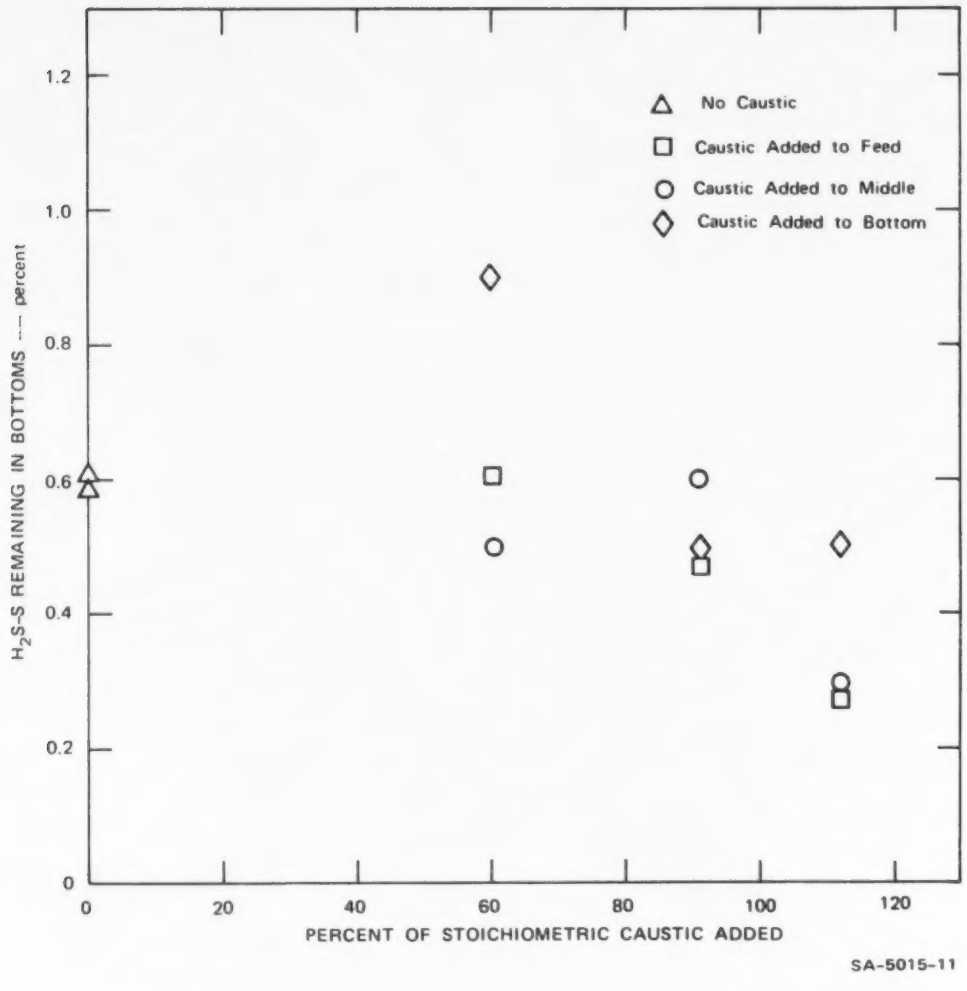

Figure 14. Refinery F: H_2S removal efficiency at 1.03 lb/gal stripping steam (fresh feed basis) with caustic added at a single point in the column.

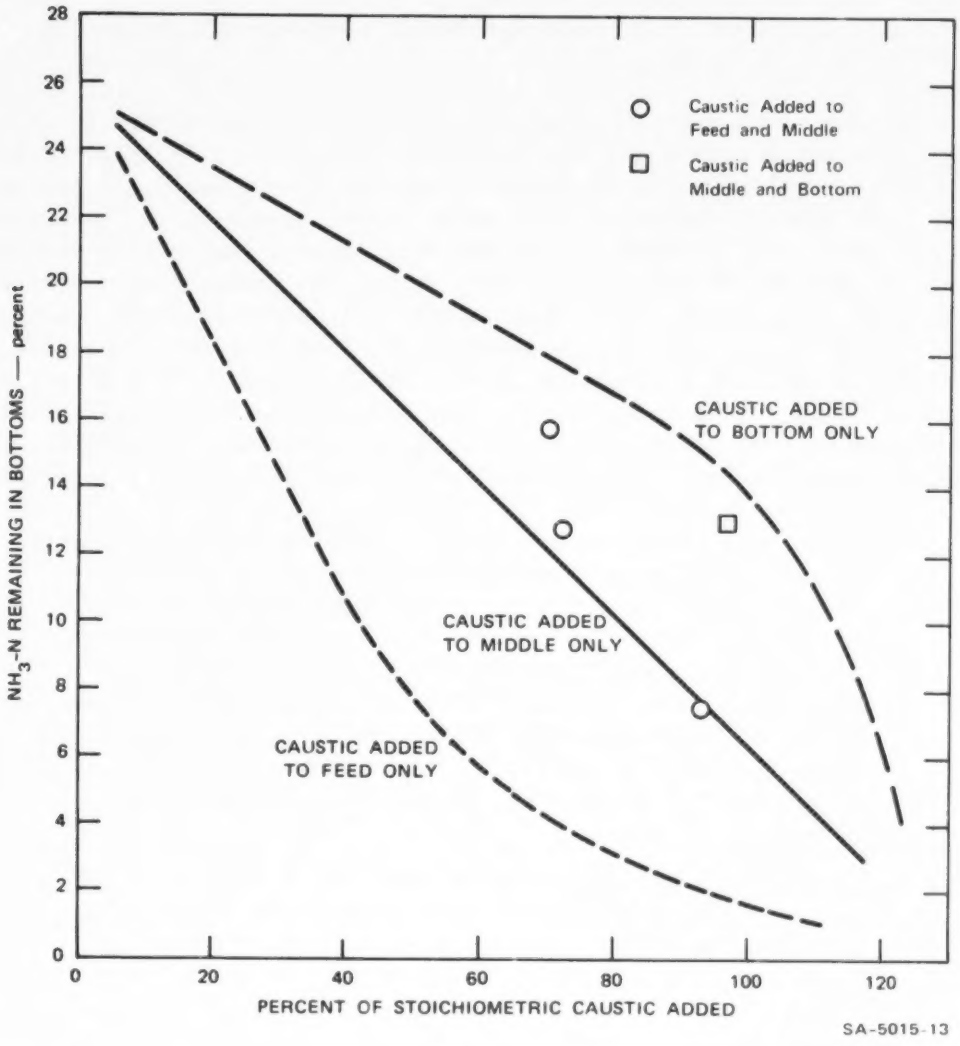

Figure 15. Refinery A: NH_3 removal efficiency at 1.03 lb/gal stripping steam (fresh feed basis) with caustic added at two points in column.

SECTION 10

SUBSTITUTION OF CAUSTIC FOR STEAM IN STRIPPING SOUR WATERS WITH LOW "FIXED" AMMONIA LFVELS

A sour water with low fixed ammonia levels contains very low levels of acidic components other than sulfides. The pH profile in a stripping column is usually highly dependent on the steam rate used. At high steam rates, we expect a pH of about 9* to be established high in the column. If the steam rate is high, all of the free ammonia and sulfide will be removed, and the pH may become acidic due to the presence of the small amount of acid. Most of the ammonia and sulfide are stripped out near the top of the column. At low steam rates, less sulfide and ammonia are removed during each stage. The pH will still be approaching 9 in the column bottom. It will approach either from the basic or acidic side, depending on the initial feed concentration of ammonia and sulfide. Adding caustic to such a feed will have the following general effects.

- Steam rate high: At low caustic addition rates the column pH will be 9, except near the bottom where it will be higher. If a small amount of fixed ammonia is present, it will be released by the caustic. As caustic addition rate is increased, the high pH region moves further up into the column. Sulfide levels in the bottom will rise as the high pH suppresses sulfide volatility on more of the column stages. The effect on bottom ammonia levels will be negligible. Therefore, care must be taken not to overdose with caustic.

- Steam rate low: Column pH will depend on feed composition. Ammonia and sulfide levels will be high and at low caustic addition rates, pH changes due to caustic addition (and thus stripping efficiency changes) will be small. As caustic addition rates are increased, the column will become basic and ammonia removal efficiency will increase while sulfide removal will decrease. At very high caustic addition rates, the column pH will be above 10 on every stage, and all ammonia will be un-ionized. At pH 10 sulfide removal efficiency will be decreased. Increases in caustic addition past this point will not change ammonia removal but will continue to decrease sulfide removal.

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*As discussed earlier, this pH of 9 was derived theoretically from a particular set of ionization equilibrium constants and Henry's Law constants. If real sour water exhibits another pH, this does not change the nature of the following discussion.

EXPERIMENTAL RESULTS

An experimental verification of these effects was conducted with sour water obtained from Refinery D. The raw sour water had a composition as follows:

H_2S (ppm):	5710
NH_3-N (ppm):	3370
pH:	9.0

Batch stripping of this sour water to pH 6.1 yielded a residual ammonia-nitrogen level of 50 ppm, or 3.6 meq/l. The residual ammonia is 1.4% of the feed ammonia. Fourteen stripping runs were made with caustic addition rates varying between 0.000 and 0.023 lb/gal of sour water feed. Total steam rates were varied between 0.48 to 1.41 lb/gal feed. Complete results are shown in Appendix D. Important features of the data are shown in Figure 16, which is a contour map of ammonia and sulfide removal efficiencies. This contour map shows the following expected features:

(1) At high steam rates (total steam rate > 0.8 lb/gal), the first amounts of caustic added release the fixed ammonia (which, based on the shape of the contour map is between 1% to 1.5% of the feed concentration). It is important to note the close agreement between the fixed ammonia level predicted by the contour map and the level predicted by the batch stripping test. Additional caustic cannot increase ammonia removal very much, but it does decrease sulfide removal efficiency dramatically.

(2) At very low steam rates, the first amounts of caustic added have small effects on both sulfide and ammonia removal. As caustic addition rate increases, sulfide removal efficiency begins to fall rapidly while ammonia removal efficiency becomes independent of caustic addition rate but highly dependent on steam rate. This is because pH is high on all column stages and because steam rate rather than ammonia volatility limits ammonia removal.

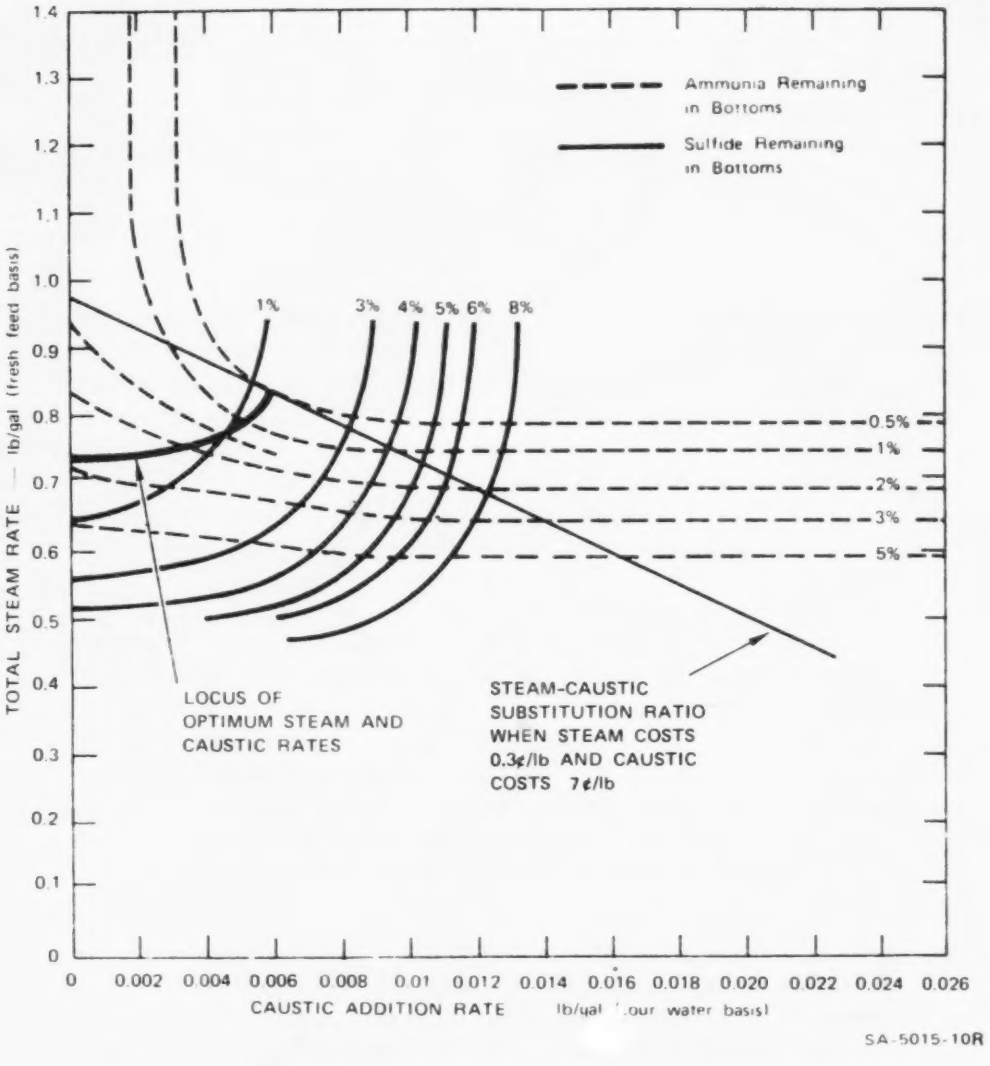
Ammonia Remaining in Bottoms
Sulfide Remaining in Bottoms
1%
3%
4%
5%
6%
8%
0.5%
1%
2%
3%
5%
LOCUS OF OPTIMUM STEAM AND CAUSTIC RATES
STEAM-CAUSTIC SUBSTITUTION RATIO WHEN STEAM COSTS 0.3¢/lb AND CAUSTIC COSTS 7¢/lb
TOTAL STEAM RATE — lb/gal (fresh feed basis)
CAUSTIC ADDITION RATE lb/gal (sour water basis)
0 0.002 0.004 0.006 0.008 0.01 0.012 0.014 0.016 0.018 0.020 0.022 0.024 0.026
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4
SA-5015-10R

Figure 16. Refinery D: Response surface of ammonia and sulfide removal efficiency versus steam and caustic addition rates.

ECONOMIC ANALYSIS

Figure 16 can be used to calculate economic optimum steam and caustic rates for achieving a target ammonia removal. The line labeled steam-caustic substitution ratio represents the combinations of steam and caustic that can be purchased for the same expenditure. For example, when steam costs $3.00/1000 lb and caustic costs 7¢/lb, the line shown represents a utility expenditure of $0.0029/gal of sour water. If we neglect changes in operating costs due to changes in cooling water usage and capital charges that result from substituting caustic for steam, two of the many possibilities for this fixed expenditure are 0.975 lb/gal of steam and no caustic, or 0.80 lb/gal steam and 0.007 lb/gal of caustic. The best ammonia removal that can be obtained for this expenditure is found where this substitution line is tangent to an ammonia level contour. The tangency is at 0.825 lb/gal of steam and 0.006 lb/gal of caustic, which yields a 0.5% ammonia level. Any other steam-caustic combination with utility costs of $0.0029/gal of sour water yields a higher ammonia level. In a similar manner, optimum combinations of steam and caustic can be developed for other utility expenditures. The lines representing other utility expenditures will be parallel to the line shown in the figure. Each of these lines will be tangent to an ammonia level contour at the optimum combination. The line connecting these tangency points is a locus of optimum steam and caustic rates. For the utility prices chosen, the locus shows that for achieving ammonia residuals of 3% or more (less than 97% removal), only steam should be used. If lower ammonia residuals are required, the economic optimum requires that caustic be used. Note, however, that the optimum utility mix of steam and caustic does degrade sulfide removal. Thus, sulfide constraints may prohibit using the optimum utility mix.

The steam cost used in Figure 16 is perhaps too high--especially in a refinery where waste heat from low pressure steam is available. Figure 17 was developed to show the optimum steam-caustic usage when steam is valued at only $0.50/1000 lb. The price of caustic was also raised to a more realistic 11¢/lb. The change is dramatic. For this feed there is no economic incentive to use caustic until better than 99% ammonia removal is required.

Different feeds would yield different results with this type of analysis, and a complete analysis would also have to include the effects of changing the number of equilibrium stages. The results with Refinery D, however, suggest that caustic is economically attractive only when very high ammonia removals are required.

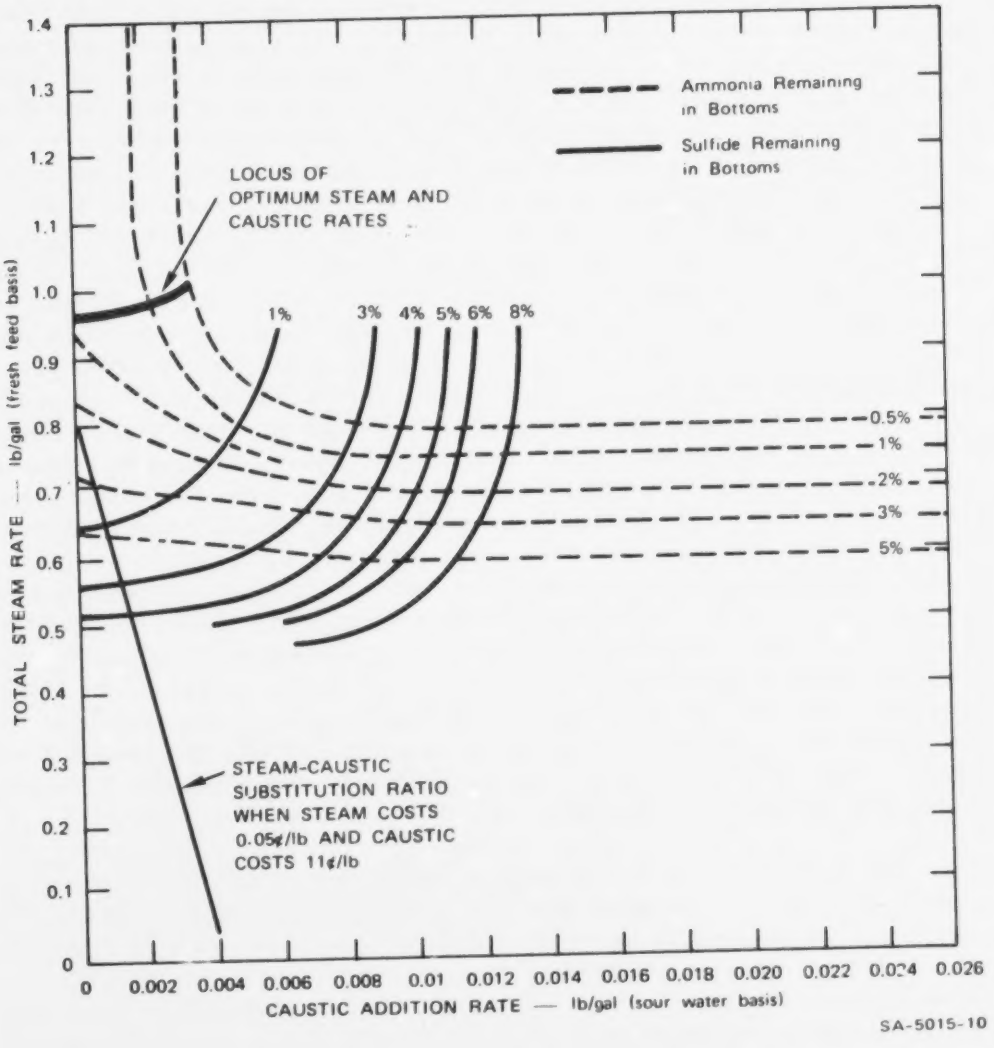

Figure 17. Refinery D: Response surface of ammonia and sulfide removal efficiency versus steam and caustic addition rates. Calculation of optimum steam-caustic rates when steam is inexpensive.

SECTION 11

BEHAVIOR OF CYANIDE COMPOUNDS DURING STRIPPING

Analysis of stripped sour water samples collected for this study indicated that the methodology for measuring cyanide in sour waters, either as free cyanide or complexed with metals, was inadequate. The principle defect was that measurements for free cyanide often showed higher results than measurements of the sum of free plus complexed cyanide. Some material in sour waters interferes with the analytical procedures.

To overcome the analytical difficulty, we used two different artificial feeds to investigate cyanide behavior during stripping. A few runs were conducted, using buffered distilled water to investigate the effects of pH and steam rate on free cyanide. A more extensive series of runs was used to investigate the behavior of free and complexed cyanide and thiocyanate in artificial sour waters prepared from ammonium hydroxide and hydrogen sulfide gas. These artificial feeds were handled carefully to avoid oxidation of the sulfide.

CYANIDE REMOVAL FROM BUFFERED SOLUTIONS

Phosphate and borate buffers and distilled water were used to prepare solutions with pH values of 7 and 9, respectively. KCN was added to bring the solution cyanide concentration to approximately 10 ppm CN^-. Cyanide levels in the feed and bottoms were measured using a colorimetric test sold by the Hach Chemical Company. The Hach procedure is adequate for solutions containing no interferences. A ten-plate column was used for these stripping runs.

Figure 18 illustrates the results. The complete run data is in Table C-1 of Appendix C. As expected, cyanide removal is sensitive both to pH and steam rate. At pH 7 it is possible to remove all the cyanide at realistic steam rates, because the cyanide is almost 100% un-ionized at this pH. At pH 9, however, cyanide removal is not complete at any reasonable steam rate. The reason for this is twofold. First, at pH 9, only 50% of the cyanide in solution is in the volatile HCN form. Second, HCN volatility is at least two orders of magnitude less than that of sulfide. This means that at a pH like 9, where sulfide stripping is

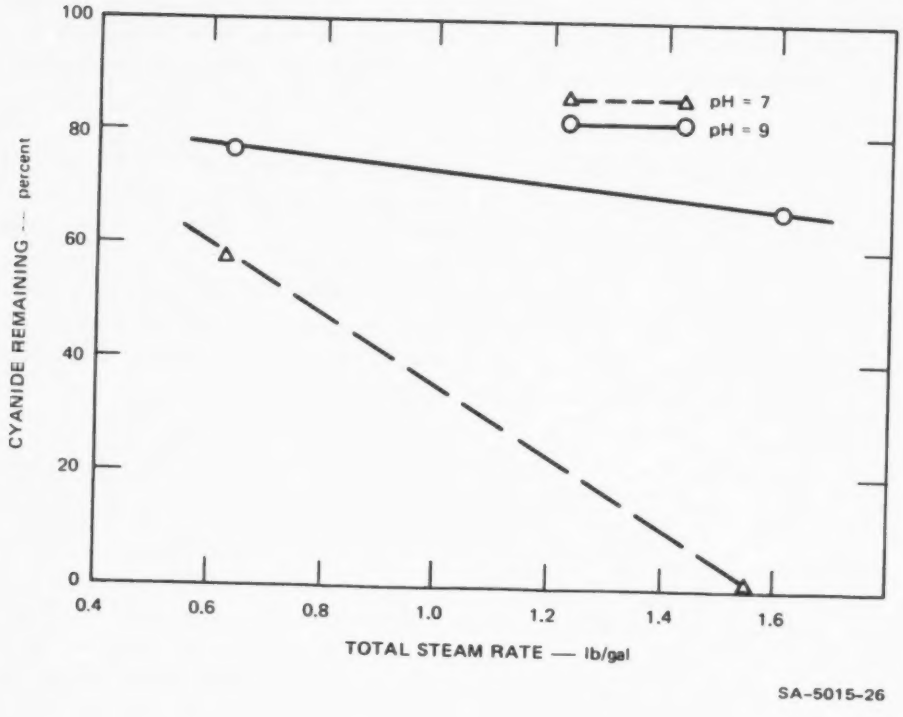

Figure 18. Steam stripping of cyanide from buffered solutions using a 10-plate column.

not impaired, even though sulfide at this pH is not all in the volatile form, cyanide stripping can be impaired. Since we expect a stripper to operate with a pH nearer to 9 than to 7, this experiment suggests that complete cyanide removal in a stripper will be difficult to achieve.

CYANIDE REMOVAL FROM ARTIFICIAL FEEDS

Artificial feeds were prepared from deaerated distilled water to prevent oxidation of sulfide, since the oxidized sulfur compounds that result are acids and would interfere with interpretation of the results. Ammonium hydroxide was added to the deaerated water and H_2S was bubbled through the solution until a specified weight change occurred. The weight change was hard to measure reproducibly, so some variance occurred in feed sulfide levels.

KCN, KSCN, and $K_3Fe(CN)_6$ were added to the freshly prepared ammonium sulfide solutions in order to obtain the equivalent of 50 ppm of CN^-. (For example, 50 ppm of CN^- requires 186.5 ppm of KSCN.) Three stripping runs were conducted with KCN as the only source of cyanide, three with KSCN as the only source, and three with $K_3Fe(CN)_6$. Both free and complexed cyanide concentrations were determined by ASTM Method A for total cyanides. The complete run data are given in Appendix C but the important features are illustrated in Figure 19. Three conclusions are clear:

(1) Complex cyanides are not significantly converted to free cyanides in the laboratory stripper and are not removed.

(2) Thiocyanate is not removed by steam stripping.

(3) Free cyanide stripping efficiencies are higher than expected. The complete run data show that for these free cyanide stripping experiments the feeds had pH values of nine and the bottoms had pH values of 10. From the results in buffered solutions, we would expect a minimum of 70% of the feed cyanide to remain in the bottoms because the alkaline pH values suppress cyanide volatility.

The temperature effect on the pH of ammonium sulfide solutions, which was discussed in Section IV, is probably responsible for the high stripping efficiency of cyanide in the artificial feeds. It is quite likely that these feeds, which showed a pH of about 9 when measured at room temperature, became more acidic when raised to stripping column temperatures. The pH in the top of the column was probably very close to 7. At this

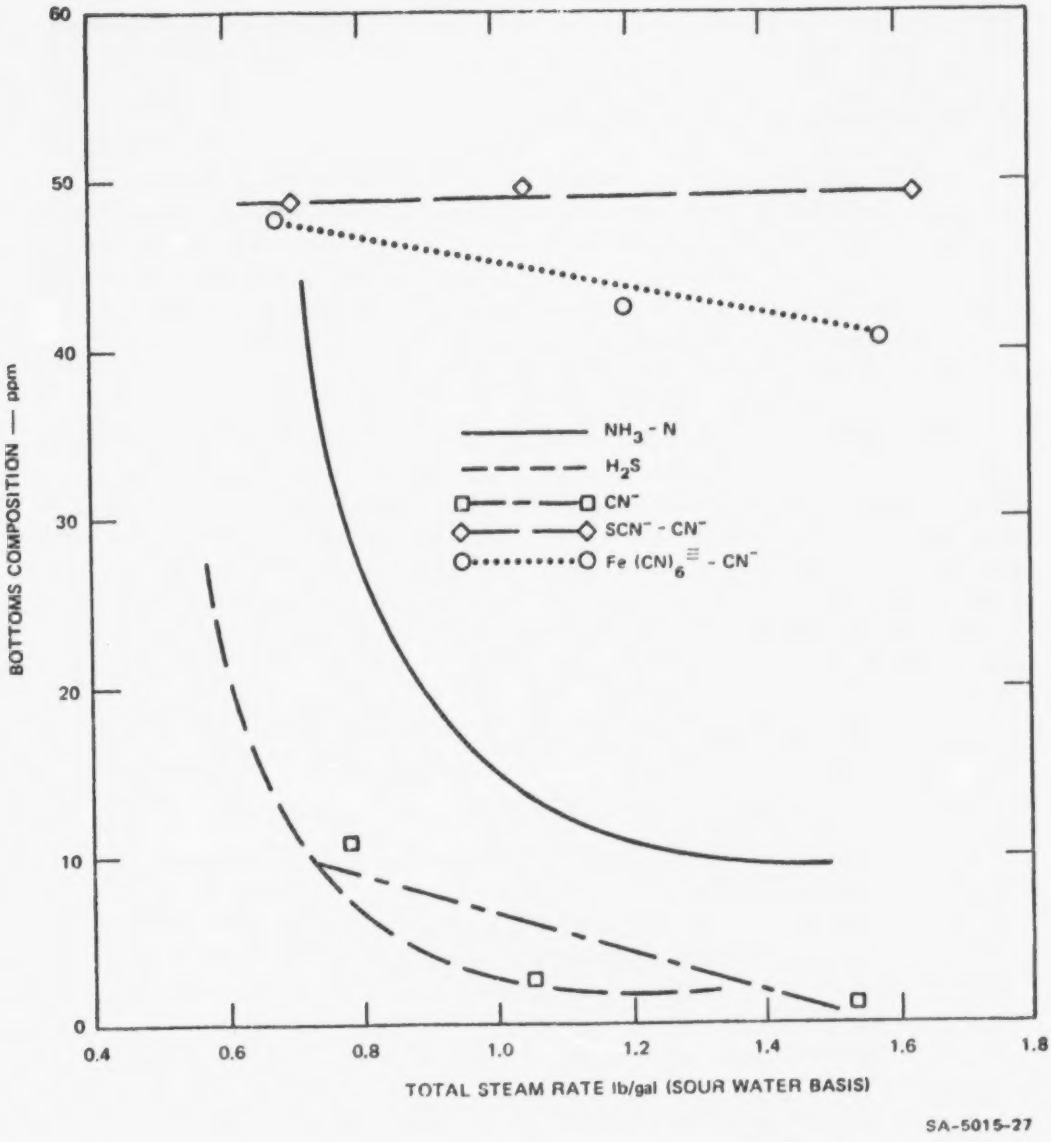

Figure 19. Steam stripping of cyanide compounds from artificial sour waters using a 10-plate column.

pH substantial cyanide stripping would occur. The buffered solutions would show far less pH change with temperature, than the artificial feeds. The cyanide solution buffered to pH 9 would remain alkaline at column temperatures and little cyanide stripping would occur.

During runs when either free or complexed cyanide was present, some cyanide was converted to thiocyanate in the stripping column. This probably means that our precautions to eliminate sulfide oxidation were not entirely successful since the chemical route to thiocyanate is through polysulfide, which is an oxidation product of hydrogen sulfide. The conversion to thiocyanate was not sufficient to explain the higher than expected cyanide removals.

On the basis of results from artificial feeds, we would expect the following results for an actual stripper operating on real sour water:

(1) Good free cyanide removal efficiency if bottoms pH does not exceed 9.

(2) Little or no removal of metal-complexed cyanides.

(3) Some conversion of feed cyanides to thiocyanate. This will be a strong possibility if polysulfides are used in the sour water system to control corrosion, or if the sour water is exposed to oxygen.

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APPENDIX A

ANALYTICAL METHODS

SULFUR COMPOUNDS

The sulfur compounds measured were free sulfur, total sulfur, thiosulfate and polythionates, sulfur dioxide, thiocyanate, and hydrogen sulfide. The sulfide analyses are discussed in the body of the report. Separate determinations of sulfate and polysulfide were not made because a reproducible method could not be developed for sour waters within the time constraints of the project.

Free Sulfur

Free sulfur has a very low solubility in water, so if a significant amount is present it will be as particles. The sample is filtered (which removes all interference from dissolved sulfur compounds), and the material on the filter is dissolved in petroleum ether. The sulfur in the petroleum ether is determined colorimetrically by its reaction with cyanide to form thiocyanate. The procedure is described in the following section ("Thiosulfate and Polythionates").

Thiosulfate and Polythionates Chemistry

These compounds are detected colorimetrically with Fe^{+3} after conversion to thiocyanate. The thiosulfate reacts with cyanide at all pH values between 4 and 14 in the presence of Cu^{+2}. Polythionates react with cyanide at all pH values ≥ 7 and do not require the Cu^{+2} catalyst. No reactions occur when $pH \ll 4$. Because of the differences in pH and catalyst requirements, thiosulfate and polythionates can be estimated separately. Also, since no reactions occur in highly acidic solution, a blank prepared by changing the order of solution addition can be used to determine the amount of thiocyanate present in the sample.

Thiosulfate

Thiosulfate can be measured without interference from polythionates by buffering the reaction mixture to pH 5. At this pH, in the presence of Cu^{++},

$$SSO_3^{=} + CN^{-} \rightarrow SCN^{-} + SO_3^{=} \quad . \qquad (1)$$

The SCN is determined colorimetrically by formation of a red complex with Fe^{+3} from $Fe(NO_3)_3$ in nitric acid. Free SCN^- in solution is determined by preparing another sample with the iron solution added first, followed by the CN^- and the Cu^{+2}. Since the iron solution is very acidic, the resultant reaction mixture has a pH $\ll 4$, and only SCN^- that was originally in the solution reacts to form the red color.

Polythionate

At neutral or basic pH, all of the polythionates react with CN^- to form SCN^-. For all of the polythionates except trithionate the reaction is rapid:

$$S_nS_2O_6^{=} + (n-1)CN^- + 2OH^- \xrightarrow{pH > 7} (n-1)SCN^- + S_2O_3^{=} + SO_4^{=} + H_2O \qquad (2)$$

After this reaction proceeds to completion (12 minutes), Cu^{++} (which causes the reaction mixture to become acidic) is added and the thiosulfate formed by reaction (2), as well as any thiosulfate originally present in the sample, reacts to form an additional amount of SCN^-. Then, correction for the thiosulfate and SCN^- originally present in the solution allows an estimate of 'n' that can be converted into polythionate (excluding trithionate) sulfur by using gravimetric factors. Alternatively, if the correction for sample thiosulfate is not made, the procedure gives an approximate value for total sulfur in polythionate (except trithionate) plus thiosulfate. The approximation is an underestimate because the $SO_4^{=}$ from reaction (2) will not be counted. For samples that are mostly thiosulfate (such as the sour waters encountered in this study), the error is not severe.

Trithionate

Trithionate behaves exactly like the other polythionates except that it reacts much more slowly. An overnight reaction time is required. Trithionates can be estimated directly by comparing the results of two determinations of polythionates: one with an overnight reaction time and the other with only a 12-minute reaction time. Trithionates were not detected in any of the sour waters sampled in this program.

METHODS FOR THIOSULFATE AND THIOCYANATE

Samples are filtered through a 0.45 μm millipore filter using positive nitrogen pressure. This removes elemental sulfur present which would yield high results for thiosulfate and thiocyanate. The filter should be saved and treated with petroleum ether to dissolve the sulfur. The resulting solution is used for free sulfur analysis.

A standard curve is prepared with each group of samples. Two concentrations are adequate along with a reagent blank.

Thiosulfate

Standards and samples are pipetted into 150-ml beakers. After addition of 5 ml of buffer solution, the samples are diluted to 30 ml. The solutions are mixed thoroughly by swirling, and 5 ml of NaCN solution is added. Then 3 ml of $CuCl_2$ solution is added immediately; the beakers are swirled vigorously during these additions. Next, 5 ml of $Fe(NO_3)_3 + HNO_3$ is added rapidly with serological pipette. The Cu^{++} and CN^- solutions are added from burettes. As quickly as possible after the addition of the Fe^{+++} reagent, the solutions are transferred to a black-painted 100-ml volumetric flask and diluted to volume. These solutions are then poured into screw-top bottles covered with aluminum foil. The sample must be protected from light. The reagent blank is prepared from distilled water using the same volume of reagent as for the sample; only the order of their addition is changed. The Fe^{+++} is added first, followed by NaCN and $CuCl_2$. The method is valid over a concentration range of 0.0 to 20 mg $S_2O_3^{2-}$.

All work should be done in a hood as HCN is evolved continuously from these solutions.

The absorbence is measured at 460 mm.

Thiocyanate

This measurement is made by adding the Fe^{+++} reagent first and the NaCN and $CuCl_2$ reagents second as in the blank. Free thiocyanate is measured by this procedure, and these values are subtracted from the thiosulfate measurements. Absorbances can be subtracted directly to yield a value, or concentrations can be used. A standard curve is prepared from NH_4SCN solution. Concentration range is from 0.05 to 1.0 mg SCN^-. No buffer is used.

Reagents

1% (w/v) NaCN Solution. Dissolve 10 gm of NaCH in 1 liter of distilled water.

Mixed ferric nitrate-nitric acid reagent. Dissolve 300 gm of $Fe(NO_3)_3 \cdot 9H_2)$ in distilled water, add 400 ml of (55%) HNO_3 solution, and dilute to 1 liter.

0.1 M $CuCl_2$ Solution. Dissolve 17.05 gm of $CuCl_2 \cdot 2H_2O$ in distilled water and dilute to 1 liter.

Buffer Solution. 10% ammonium acetate in solution. The pH of this solution is adjusted to 5 with ammonia or acetic acid.

METHODS FOR HYDROGEN SULFIDE

The sour water samples contain materials that interfere with the methylene blue color method. Cadmium hydroxide is used to precipitate the sulfide and separate it from the interferences. The solution is adjusted to a phenolphthalein end point. Most samples are already alkaline. After pH adjustment, 2 ml of NaOH solution and 5 ml of cadmium solution is added. The samples are vigorously mixed and centrifuged to bring down the CdS and $Cd(OH)_2$ formed. The liquid is decanted from the samples and the precipitates are transferred to a 25-ml volumetric flask with 15 ml of water. Then, 3 ml of the amine reagent is added down the side of the flask, without stirring; 0.1 ml of the iron solution is added quickly; and the flask is stoppered and mixed. A period of 20 minutes is allowed for color development and the samples are read in a colorimeter at 670 nm. The method is valid over a total H_2S range of 1 μg in the sample.

Solutions

Mix 50 ml of concentrated H_2SO_4 and 30 ml of water; when the solution is cool, dissolve into it 10.5 g of n,n-dimethyl-p-phenylenediamine oxalate. A 25-ml portion of this solution is diluted to 1 liter with 1:1 H_2SO_4. This solution is stable and is used for color development.

Ferric Chloride Solution--Dissolve 100 gm of $FeCl_3 \cdot 6H_2O$ in water and dilute to 100 ml.

NaOH--1 gm per liter is used for pH adjustment and to make solutions alkaline.

Cadmium Acetate--Dissolve 3 gm of $Cd(C_2H_3O_2)_2 \cdot 2H_2O$ in water and dilute to 1 liter.

Standard Sulfide Solution--Dissolve 35.28 gm of $Na_2S \cdot 9H_2O$ in oxygen-free water and dilute to 1 liter. This solution is standardized by iodometric titration.

METHODS FOR SULFUR DIOXIDE

Sulfur dioxide is measured directly in the sour water. An aliquot of 0.5-8 ml is used depending on the concentration. The sample is added to a 15-ml Erlenmeyer flask and water is added to increase the volume to 8 ml. Then 1 ml of p-rosaniline solution is added. The samples are swirled to mix and 1 ml of formaldehyde solution is added. A period of 20 minutes is allowed for color development. The sample is read against DI water. A reagent blank is read and the absorbence is subtracted from all sample readings. Absorbence is measured at 560 mm. Standard solutions and concentrations are from 5 to 20 μg per ml. Graduated pipettes are used throughout.

Solutions

Standards are made up from a solution of Na_2SO_3. Solutions are stabilized by use of sodium tetrachloromercurate.

P-Rosaniline Solution. Mix 4 ml of a 1% aqueous solution of p-rosaniline and 6 ml of concentrated HCl and dilute to 100 ml.

Formaldehyde Solution. Dilute 5 ml of 40% formaldehyde to 1 liter with DI water.

Sodium Tetrachloromercurate Solution. Add 27.2 gm mercuric chloride and 117 gm of NaCl to a 1-liter flask and dilute to volume.

METHODS FOR TOTAL SULFUR

Total sulfur is determined by an alkaline permanganate oxidation of all sulfur species to sulfate, which is determined gravimetrically. The alkaline method was chosen to avoid volatilization of sulfides.

An aliquot of 50-100 ml of sour water is pipetted into a casserole dish for concentration. Two ml of 50% NaOH is added and the sample is evaporated in a steam bath. Then the sample is concentrated to 15 ml, and

saturated $KMnO_4$ is added until the purple color persists. A glass rod is used to stir the solution. The sample is evaporated to dryness in the steam bath and is then ignited in a muffle furnace at 600°C for 2 hours. The casserole still contains the short glass stirring rod used to mix the $KMnO_4$ and the sample.

After the ignition, the casserole is cooled and covered with a watch glass, and concentrated HCl is added until the brown residue is dissolved. The solution is then digested until it is clear and pale yellow. The watch glass is put in a vertical position, and the sample is evaporated to dryness. The residue at dryness should be white in color. If it is not, the dehydration from concentrated HCl is repeated.

Concentrated HCl (5 ml) is added to the residue, followed by 25 ml of deionized water. This is mixed and heated to incipient boil in order to precipitate silica that was leached from the glassware under the alkaline conditions of the oxidations. This mixture is stirred and filtered into a 400-ml beaker through Whatman 42 or equivalent filter paper. It is then washed eight times with deionized water, after which the silica material and filter paper are discarded. The solution is diluted to 300 ml, and methyl orange indicator is added; color will be red. The beaker is covered with a watch glass and heated in a steam bath until condensation appears on the watch glass. Then 5 ml of 10% $BaCl_2$ solution is added and the mixture is stirred vigorously. Samples are digested overnight on the edge of the steam bath. The mixture is then filtered through medium-porosity Selas crucibles and washed with hot water six times. The crucibles are ignited in a muffle furnace at 900°C for 1 hour; after which they are dessicated and weighed. The tare weight minus the sample weight equals the weight of $BaSO_4$. This weight times the gravimetric factor 0.13735 equals the weight of the sulfur present in the original sample.

NITROGEN COMPOUNDS

The nitrogen compounds measured were total Kjeldahl nitrogen (TKN), ammonia, and free and total cyanides, TKN was measured using procedures described in Standard Methods (1976). The ammonia and cyanide methods are discussed in the body of the report.

Total Kjeldahl Nitrogen

An unfiltered 25-ml sample of Kjeldahl nitrogen is pipetted into 50 ml of Kjeldahl digestion flash. Then 6 ml of EPA digestion solution is added.* A blank mixture is run with 25 ml of deionized water following the same procedure. The sample is put on a micro Kjeldahl digestion unit and heated at full heat. If foaming occurs, the heat should be reduced until the sample has evaporated to a minimum volume. The sample is digested until it is clear and has no color and until SO_3 fumes are visible as heavy white vapor. The heat is turned off and the sample is cooled in place. When cool, the sample is transferred to a 100-ml volumetric flask and diluted to volume. The samples are then poured into 10oz plastic bottles with screw top lids. Each bottle contains a magnetic stirring bar. When all samples in a series are complete to this point, a series of standards is prepared. Concentrations of 10, 50, and 100 ppm of nitrogen, respectively, are prepared. Then 6 ml of the digestion solution is added to each of the standards and they are diluted to a 100-ml volume and transferred to plastic bottles. To each of the plastic bottles is added 5 ml of a solution of 10 M NaOH and 2 N NaI. The procedure for making this solution is in the Orion NH_3 specific ion book. The samples are capped tightly immediately after the base addition. They are then swirled to mix and cooled to room temperature in a water bath. The specific ion electrode is then calibrated with the standards and the sample concentrations are read directly from the meter scale. Standards are good for 8 hours when bottles are kept tightly capped. A magnetic stirrer is used during the measurements, and the meter should come to a steady state in 15-20 seconds.

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* For EPA digestion solution, 267 gm of K_2SO_4 is dissolved in 1300 ml of distilled water, and 400 ml of concentrated H_2SO_4 is added. When the solution is cool, sulfate solution is added and diluted to 2 liters with water. For mercuric sulfate solution, 8 gm of red HgO is dissolved in 50 ml of 1:5 H_2SO_4 and the solution is diluted to 100 ml with distilled water.

HEAVY METALS AND ALKALINE EARTH ELEMENTS

Heavy metals and alkaline earth elements were measured by a two-step procedure. For a preliminary determination, samples were evaporated to dryness and pyrolyzed in a muffle furnace. The residual was scanned with spark emission spectroscopy to obtain semiquantitative estimates of the major elements present. Detailed and quantitative estimates were obtained by atomic absorption spectroscopy. The flame conditions and instrument sensitivity for the elements measured are tabulated below.

Metal	Flame	Optimum Working Range (μg/ml)	Sensitivity (μg/ml)	Wavelength (nm)
Na	Air-Acetylene	0.15-0.60	0.003	589.0
Ca	Nitrous Oxide Acetylene	1-4	0.021	422.7
Mg	Air-Acetylene	0.1-0.4	0.003	285.2
Cr	Air-Acetylene	2-8	0.055	357.9
V	Nitrous-Oxide Acetylene	40-120	0.88	318.5
Fe	Air-Acetylene	2.5-10	0.062	248.3
Cu	Air-Acetylene	2-8	0.04	324.7

The methods used to suppress interferences with metal measurement are tabulated below.

Metal	Control of Interferences
Na	Use ionization suppressant.
Ca	Use ionization suppressant and release agent.
Mg	Use release agent or nitrous oxide-acetylene flame.
Cr	Use oxidizing air-acetylene flame or nitrous oxide-acetylene flame.
V	Enhancement of signal is stabilized by excess aluminum.
Cu	Depression of signal at high Zn/Cu ratios is overcome by lean air-acetylene or nitrous oxide-acetylene flame.

APPENDIX B

WEAK ACID TITRATION CURVES
(REFINERIES A, D, F)

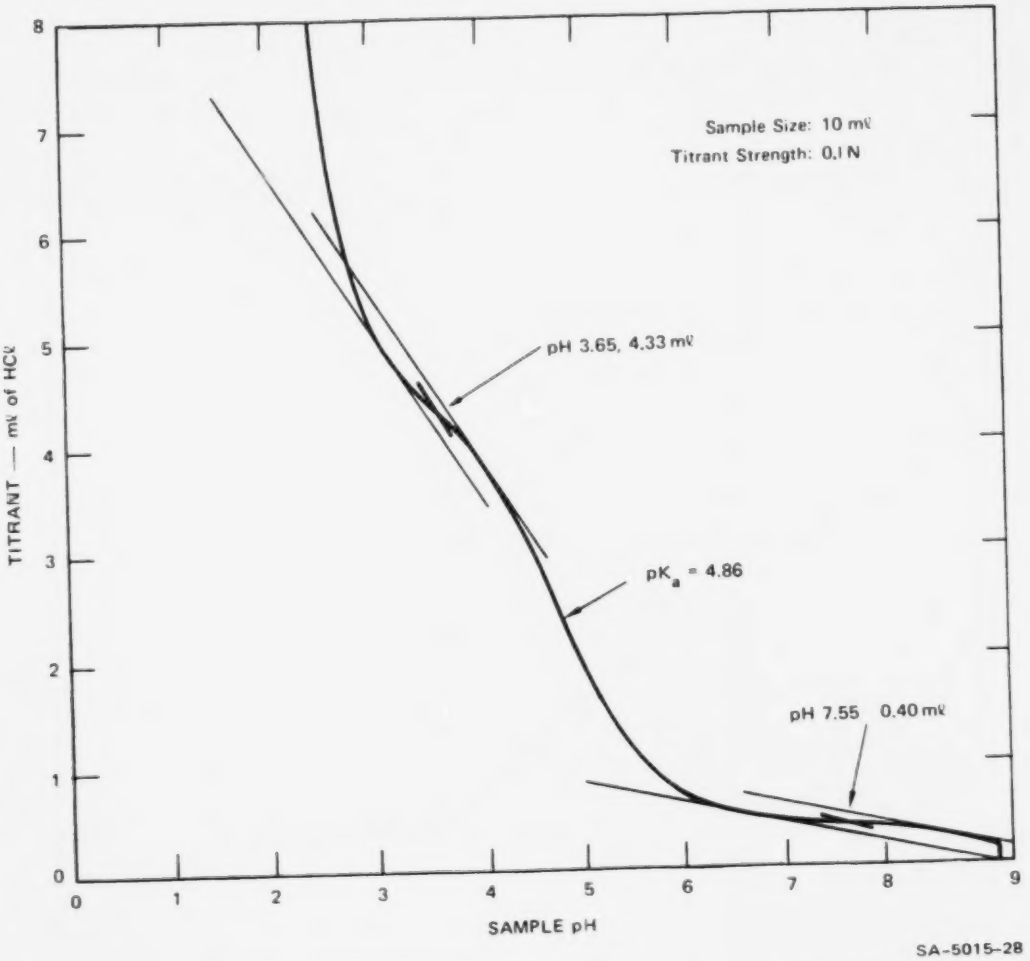

Figure B-1. Potentiometric titration of stripped sour water from Refinery A: (sample No. A3)

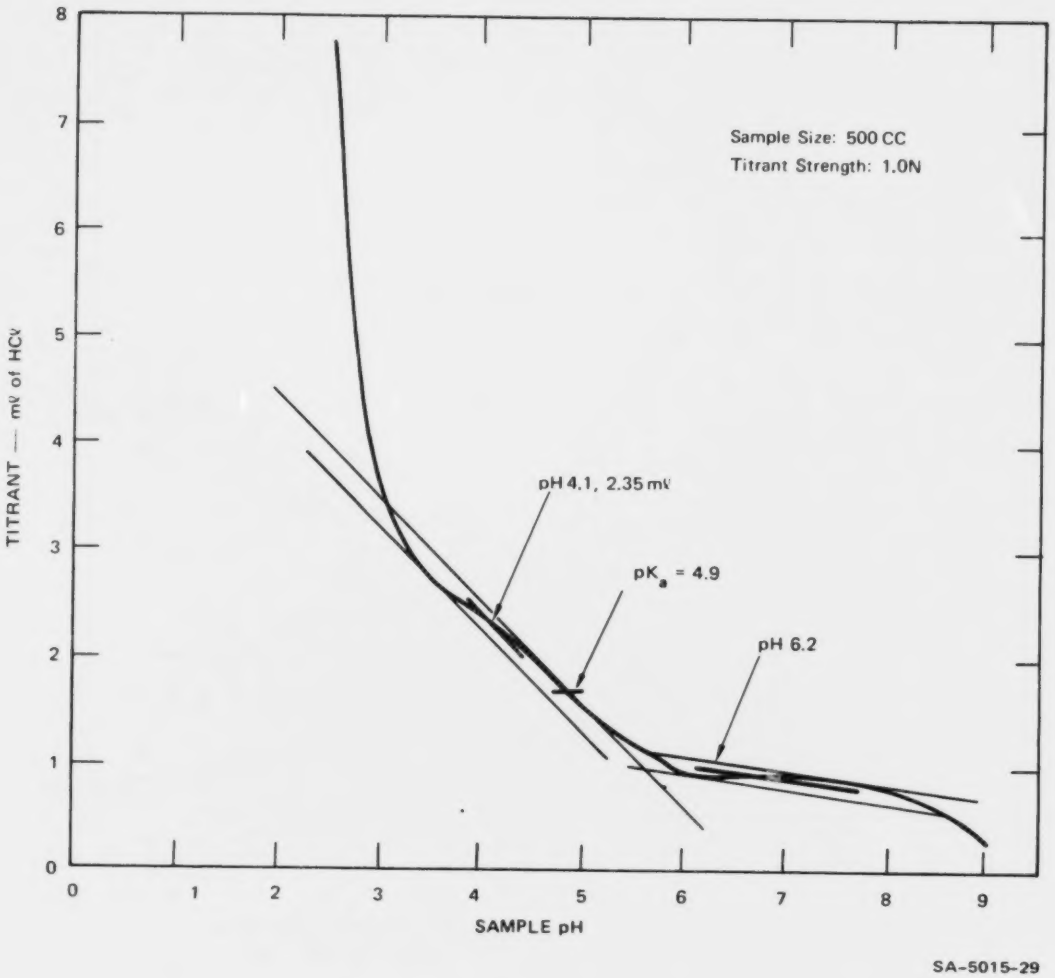

Figure B-2. Potentiometric titration of stripped sour water from Refinery D.

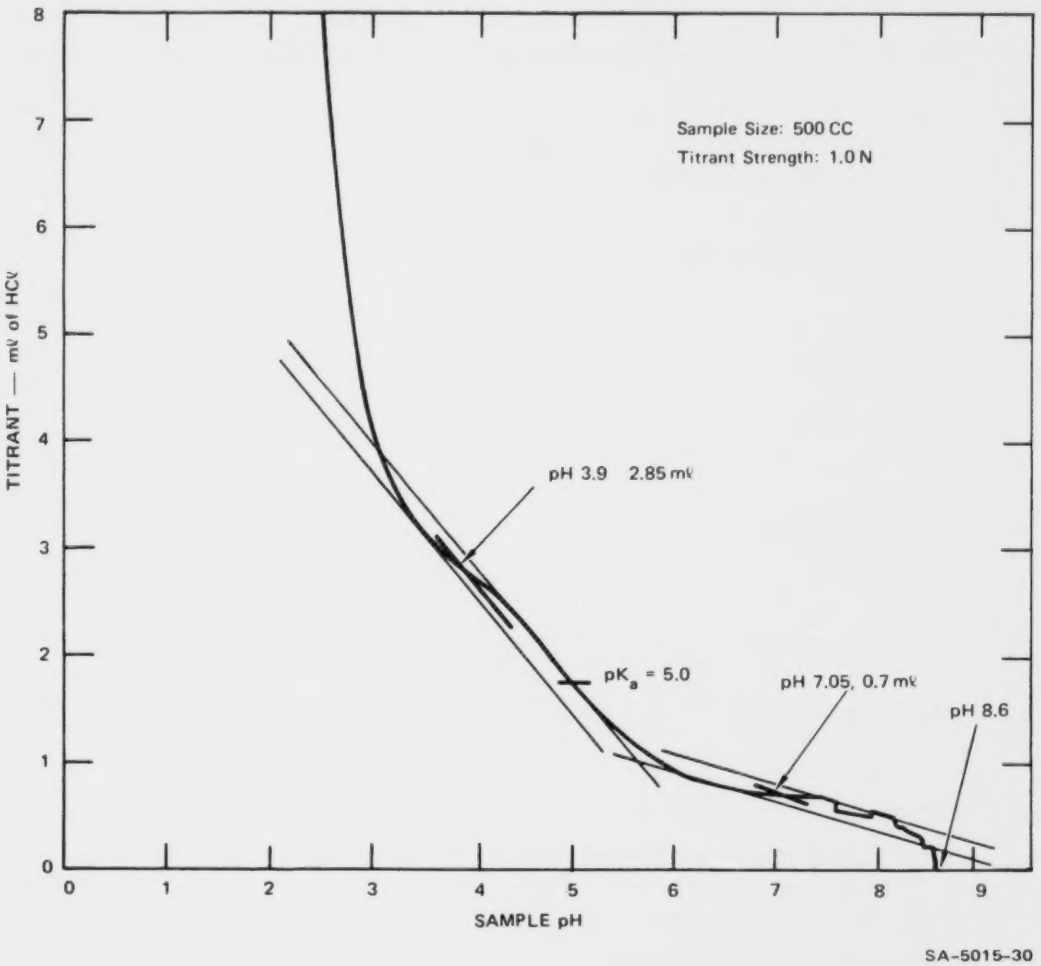

Figure B-3. Potentiometric titration of stripped sour water from Refinery F.

APPENDIX C

STRIPPING OF ARTIFICIAL FEEDS CONTAINING CYANIDES

TABLE C-1. CYANIDE STRIPPING TESTS IN BUFFERED WATER

	Run Number			
	1	2	5	6
Steam*				
Stripping steam (lb/gal fresh feed)	1.11	0.96	0.42	0.41
Total steam (lb/gal fresh feed)	1.55	1.61	0.63	0.64
Feed				
CN (ppm)†	9.5‡	12§	12‡	13§
pH	7	9	7	9
H_2S (ppm)	0	0	0	0
NH_3	0	0	0	0
Bottoms				
CN (ppm)†	<0.02	8	7	10
pH	7	9	7.1	8.9
Efficiency (%)	~100%	33%	42%	23%
Temperatures				
Reflux (^oF)**	180	150	160	174
Feed (^oF)	150	150	170	172

*Stripping steam is the amount of steam leaving the feed tray. Total steam is the total steam fed to the column minus the steam equivalent of column heat losses.

†Measured by Hach colorimetric procedures.

‡Solution was 0.005 M $Na_2H\ PO_4$, 0.005 M NaH_2PO_4.

§Solution was 0.005 M $Na_2B_4O_7$.

**See Table on p. H-2 for conversion to ^oC.

TABLE C-2. STEAM STRIPPING OF CYANIDE COMPOUNDS FROM ARTIFICIAL FEEDS

		Run Number								
		1021-3	1022-5	1022-4	1028-9	111-11	1029-10	1027-8	1026-6	1027-7
Steam *										
Stripping steam (lb/gal fresh feed)		0.33	0.61	1.09	0.26	0.60	1.19	0.26	0.72	1.11
Total steam (lb/gal fresh feed)		0.78	1.05	1.54	0.70	1.06	1.65	0.68	1.19	1.58
Feed										
NH_3-N	(ppm)	1700	1500	1700	1700	1500	1600	1600	1400	1600
H_2S	(ppm)	1122	1496	1356	1332	1600	2150	1519	2010	1402
CN^-	(ppm)	50	50	50	0	0	0	0	0	0
SCN^- as CN^-	(ppm)	0	0	0	50	50	50	0	0	0
$Fe(CN)_6^{\equiv}$ as CN^-	(ppm)	0	0	0	0	0	0	50	50	50
pH		9.2	9.5	9.6	9.8	9.8	9.5	9.9	9.5	9.9
Bottoms										
NH_3-N	(ppm)	46	<10	<10	42	<10	<10	38	<10	<10
H_2S †	(ppm)	12	5	5	4	<0.1	<0.1	23	<0.2	<0.1
CN^- †	(ppm)	11.5	2.4	1.3	0	0	0	--	--	--
SCN^- as CN^- †	(ppm)	6.4	5.2	1.3	49	50	49	3.6	6.2	4.1
$Fe(CN)_6^{\equiv}$ as CN^- †	(ppm)	0	0	0	0	0	0	48.	43.	41.
Σ CN^-	(ppm)	17.9	7.6	2.6	49	50	49	51.6	49.2	45.1
pH		10.1	10.5	10.8	9.9	8.7	8.1	10.1	8.9	8.2
Temperatures										
Feed (°F)		--	156	160	154	155	154	160	152	154
Reflux (°F)		--	171	180	155	163	175	161	170	175

*Stripping steam is the amount of steam leaving the feed tray. Fresh feed includes any water added with the caustic. Total steam is the total steam fed to the column minus the steam equivalent of column heat losses.

†Measuring by tentative ASTM Methods A and F.

APPENDIX D

STRIPPING OF SOUR WATER FROM REFINERY D TO STUDY THE EFFECT OF SUBSTITUTING CAUSTIC FOR STEAM

The data in Table D-1 were analyzed by least squares techniques to develop regressions for the percent of sulfide and ammonia remaining in the bottoms as a function of both steam and caustic rates. The regressions found were

$$\%H_2S\text{-}S = a_1 + a_2X_1^{-1} + a_3X_1^{-2} + a_4X_2 + a_5X_2^{2}$$

$$\%NH_3\text{-}N = b_1 + b_2X_1^{-1} = b_3X_1^{-2} + b_4X_2 + b_5X_2^{2}$$

where X_1 is the total steam rate in lb/gal and X_2 is the caustic addition rate. The constants and their 95% confidence limits were;

a_1	4.1 ± 6.5	b_1	11.4 ± 6.5
a_2	-8.7 ± 12.0	b_2	-22.1 ± 11.9
a_3	4.6 ± 5.1	b_3	11.6 ± 5.2
a_4	-131.5 ± 411.0	b_4	-224 ± 202
a_5	51414 ± 32257	b_5	7052 ± 8887

Both of the regressions are significant at the 0.2% level. Since, however, both regressions contain many coefficients whose 95% confidence interval includes zero, a more correct treatment of the data might require a different equation form. The correlations are both defective in that they yield negative values at some steam and caustic rates, which results in very low ammonia and sulfide residuals. Figures D-1 and D-2 show both the regression predictions and the basic data in the region of steam and caustic rates where the correlations do not yield negative values. In this region, the agreement between prediction and actual data appears to be quite good. The data in these two figures were used to generate contour maps of ammonia and sulfide removal efficiency as a function of steam and caustic rates.

TABLE D-1. REFINERY D: BENCH SCALE STRIPPING TO DETERMINE EFFECT OF VARYING CAUSTIC AND STEAM RATES

	Run Number													
	1122-2	1118-10	1122-13	1112-1	1122-14	1118-8	1118-9	1117-7	1119-11	1119-12	1115-3	1116-4	1116-5	1117-6
Steam*														
Stripping steam (lb/gal fresh feed)	1.01	0.97	0.99	0.56	0.48	0.47	0.44	0.43	0.30	0.33	0.23	0.13	0.17	0.11
Total steam (lb/gal fresh feed)	1.37	1.30	1.41	0.85	0.80	0.81	0.75	0.77	0.61	0.65	0.60	0.50	0.48	0.48
Caustic														
lb NaOH/gallon sour water	0.0	0.0124	0.0062	0.0000	0.0063	0.0124	0.0186	0.0227	0.0124	0.0185	0.000	0.0130	0.0194	0.0231
Feed														
H_2S (ppm)	6112	5586	6054	5925	5925	5890	5563	6253	5364	5574	5984	5318	5516	6018
NH_3-N (ppm)	3500	3300	2900	3600	2800	3500	3300	--	3200	3300	3700	3500	3600	3600
pH	8.8	9.0	9.1	8.9	9.1	9.1	9.0	8.8	9.1	9.2	9.2	9.2	9.2	8.7
Bottoms														
H_2S (ppm)	22	374	64	17	108	358	771	1071	508	994	119	1667	1242	1353
NH_3-N (ppm)	44	2	2	65	9	13	11	25	150	120	900	812	1200	1260
pH	7.8	10.9	10.3	9.0	10.3	10.6	11.0	11.0	10.9	11.2	10.1	11.0	11.0	10.7
H_2S remaining %†	0.4	6.5	1.1	0.3	1.9	6.2	13.3	18.5	8.8	17.2	2.1	28.9	21.4	23.4
NH_3 remaining %‡	1.3	0.1	0.1	1.9	0.3	0.4	0.3	0.7	4.5	3.6	26.7	24.1	35.5	37.4
Temperatures														
Feed (°F)	158	156	155	159	157	155	159	156	158	155	155	156	160	155
Reflux(°F)	178	178	178	173	160	160	159	162	169	170	160	168	154	163

* Stripping steam is the amount of steam leaving the feed tray. Total steam is the steam fed to the column minus the steam equivalent of column heat losses. Fresh feed includes any water added with the caustic.

† Based on average Feed composition of 5791 ppm H_2S.

‡ Based on average feed composition of 3370 ppm NH_3-N.

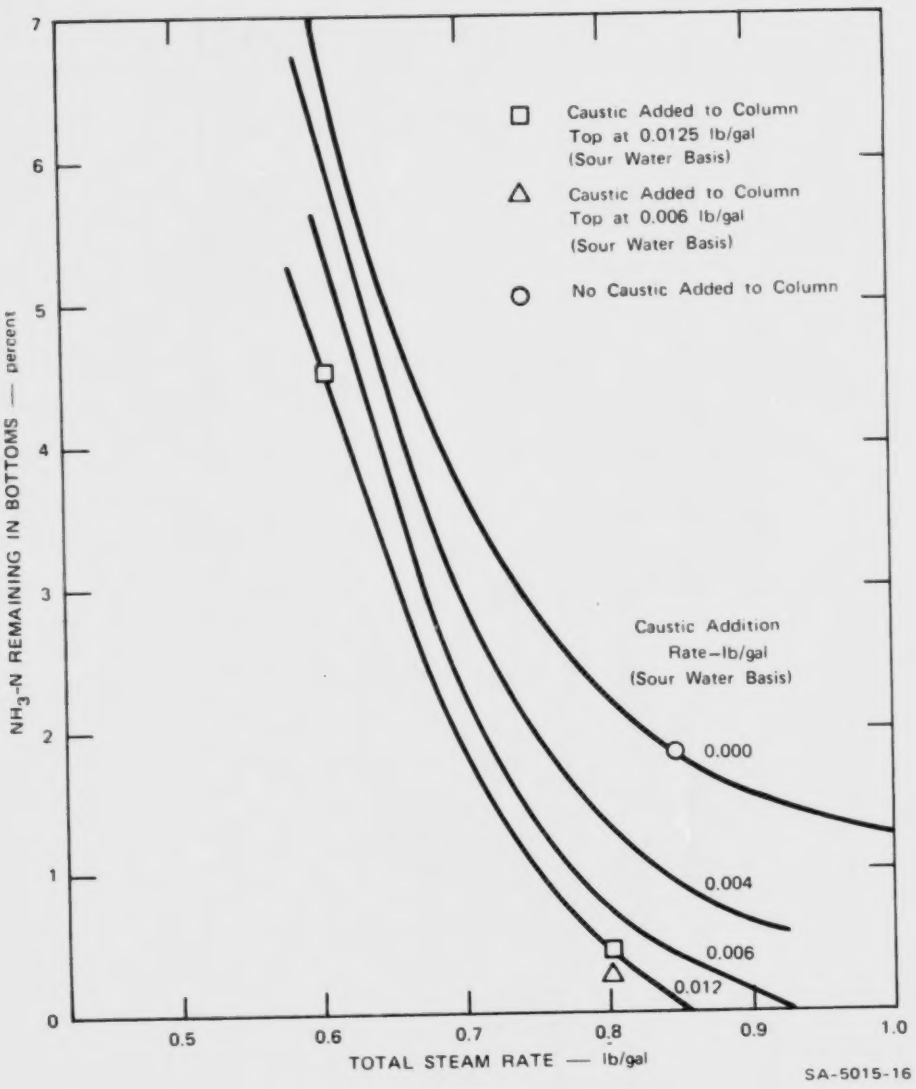

Figure D-1. Refinery D: Ammonia removal efficiency as a function of steam and caustic addition rate.

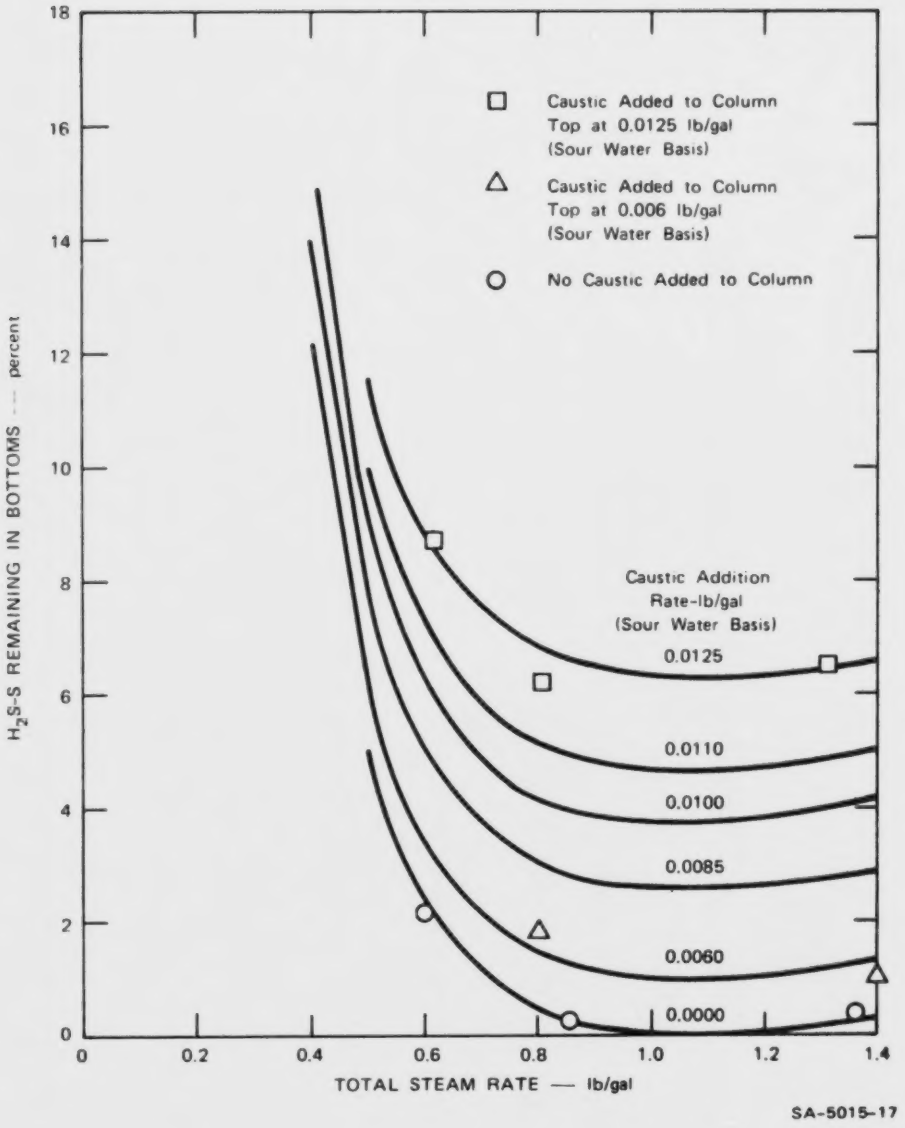

Figure D-2. Refinery D: Sulfide removal efficiency as a function of steam and caustic addition rate.

APPENDIX E

CAUSTIC ADDITION TO FREE FIXED AMMONIA (REFINERIES A, C, AND F)

TABLE E-1. BENCH SCALE STRIPPING RUNS WITH SINGLE CAUSTIC INJECTION POINT

	Caustic Injection Point												Runs not Receiving Caustic	
	Feed				Middle				Bottom					
	Run 913-1	Run 920-1	Run 106-9	Run 921-2	Run 914-2	Run 924-4	Run 927-6	Run 107-10	Run 924-5	Run 921-3	Run 106-8	Run 105-7	Run 913-0	Run 107-11
Steam*														
Stripping steam (lb/gal fresh feed)	0.94	0.92	1.01	1.15	1.15	1.28	1.10	0.97	0.98	0.91	1.10	0.97	0.93	1.02
Total steam (lb/gal fresh feed)	1.20	1.24	1.35	1.48	1.47	1.63	1.41	1.30	1.28	1.24	1.44	1.31	1.30	1.37
Caustic														
Stoichiometric dose (%)†	113	103	90	53	50	130	94	88	50	122	98	48	0	0
Addition rate (lb NaOH/gal sour water)	0.017	0.016	0.014	0.008	0.008	0.020	0.014	0.013	0.008	0.019	0.015	0.007	0	0
Feed														
H_2S (ppm)	--‡	--	3428	--	--	3462	3550	2961	--	2784	3428	2805	--	2961
NH_3-N (ppm)	3250	3200	3200	3200	3250	3550	3450	3200	3550	3100	3200	3100	3250	3200
pH	8.6	8.3	8.6	8.7	8.4	8.5	8.6	8.9	8.5	8.7	8.6	8.7	8.6	8.9
Bottoms														
H_2S (ppm)	--‡	26	5.1	30	--	27	28	15	18.5	20	17	21	--	0.5
NH_3 (ppm)	16	40	144	250	200	18	280	320	400	182	470	650	800	880
pH	10	9.6	8.25	7.0	6.8	10.7	9.3	8.8	7.3	9.8	9.4	8.9	6.4	6.5
H_2S remaining (%)§	--	0.8	0.2	0.9	--	0.9	0.9	0.5	0.6	0.6	0.5	0.7	--	0.0
NH_3 remaining (%)	0.5	1.2	4.4	7.6	6.1	0.6	8.6	9.8	12.2	5.6	14.4	19.9	24.5	26.9
Temperatures														
Feed (°F)	168	162	162	164	160	155	162	160	168	162	156	159	166	158
Reflux (°F)	173	160	167	162	164	166	166	161	170	162	160	160	170	168

*Stripping steam is the amount of steam leaving the feed tray. Fresh feed includes any water added with the caustic. Total steam is the total steam fed to the column minus the steam equivalent of column heat losses.

†Ammonia residual is 640 ppm NH_3-N or 45.7 meg/l. 45.7 meg/l is the 100% stoichiometric addition rate.

‡H_2S not reported because measurement not reliable.

§Based on an average feed concentration of 3172 ppm H_2S and 3264 ppm NH_3-N.

TABLE E-2. REFINERY A: BENCH SCALE STRIPPING RUNS WITH MULTIPLE CAUSTIC INJECTION POINTS

	Caustic Injection Points			
	Feed-Middle Run (1013-15)	Feed-Middle Run (1013-14)	Feed-Middle Run (1012-13)	Middle-Bottom Run (1011-12)
Steam*				
Stripping Steam (lb/gal fresh feed)	1.27	1.31	1.45	1.25
Total steam (lb/gal fresh feed)	1.07	1.03	1.12	0.92
Caustic				
Stoichiometric dose (%)†	94	50	52	96
Addition rate (lb NaOH/gal sour water)	0.0143	0.0077	0.0080	0.0147
Feed				
H_2S (ppm)	2727	2727	2493	3428
NH_3-N (ppm)	3800	3700	3100	3600
pH	8.9	9.0	8.7	8.9
Bottoms				
H_2S (ppm)	2	0.5	1	20
NH_3-N (ppm)	220	520	420	420
pH	8.8	7.0	6.9	9.6
H_2S remaining (%)‡	0.1	0.0	0.0	0.6
NH_3 remaining (%)	6.7	15.9	12.9	12.9
Temperatures				
Feed (°F)	168	165	154	161
Reflux (°F)	167	170	167	168

*Stripping steam is the amount of steam leaving the feed tray. Fresh feed includes any water added with the caustic. Total steam is the total steam fed to the column minus the steam equivalent of column heat losses.

†Ammonia residual is 640 ppm NH_3-H or 45.7 meq/l. 45.7 meq/l is the 100% stoichiometric addition rate.

‡Based on an average feed concentration of 3172 ppm H_2S and 3264 ppm NH_3-N.

TABLE E-3. REFINERY C: BENCH SCALE STRIPPING RUNS WITH SINGLE POINT CAUSTIC INJECTION

	Caustic Injection Points										Runs Not Receiving Caustic	
	Feed				Middle			Bottom				
	Run 126-11	Run 126-12	Run 1130-2	Run 123-9	Run 121-4	Run 122-7	Run 122-6	Run 121-5	Run 122-8	Run 121-3	Run 1129-1	Run 123-10
Steam[1]												
Stripping steam (lb/gal fresh feed)	1.05	1.01	1.05	1.09	1.04	1.05	1.03	1.05	1.07	1.08	0.95	1.00
Total steam (lb/gal fresh feed)	1.50	1.44	1.42	1.52	1.47	1.47	1.46	1.46	1.48	1.43	1.32	1.42
Caustic												
Stoichiometric dose (%)[2]	109	90	90	62	109	90	62	106	90	61	0	0
Addition rate (lb/gal sour water)	0.0013	0.0011	0.0011	.0007	0.0013	0.0032	0.0007	0.0013	0.0032	0.0007	0	0
Feed												
H_2S (ppm)	3529	3529	3498	3182	3517	3471	3439	3475	3397	3077	2828	3405
NH_3-N (ppm)	1700	1600	2000	1800	2000	2200	2200	2000	2000	2000	2000	1800
pH	8.9	8.8	8.7	8.8	8.5	8.5	8.5	8.5	8.5	8.7	8.7	8.8
Bottoms												
H_2S (ppm)	1.9	8.9	7.6	2.6	1.7	2.8	2.3	2.0	10.7	2.5	8.7	9.1
NH_3-N (ppm)	10	14	16	16	26	19	29	30	27	42	55	36
pH	9.5	8.0	8.7	8.7	9.4	8.9	6.4	9.3	9.3	9.0	--	7.6
H_2S remaining (%)[3]	0.0	0.3	0.2	0.1	0.0	0.1	0.1	0.1	0.2	0.1	0.3	0.3
NH_3 remaining (%)	0.5	0.7	0.8	0.8	1.3	0.9	1.5	1.5	1.4	2.2	2.8	1.8
Temperatures												
Feed (°F)	153	155	160	155	155	154	155	156	157	165	158	156
Reflux (°F)	170	170	173	168	168	169	167	167	170	178	176	174

1/Stripping steam is the amount of steam leaving the feed tray. Total steam is the steam fed to the column minus the steam equivalent of column heat losses. Fresh feed includes any water added with the caustic.

2/Ammonia residual is 50 ppm NH_3-N or 3.57 meq/1. 3.57 meq/1 is the 100% stoichiometric caustic addition rate.

3/Based on an average feed composition of 3362 ppm H_2S and 1942 ppm NH_3-N.

TABLE E-4. REFINERY F: BENCH SCALE STRIPPING RUNS WITH SINGLE CAUSTIC INJECTION POINT

	Caustic Injection Points									Runs Not Receiving Caustic	
	Feed			Middle			Bottom				
	Run 1223-2	Run 1229-10	Run 1228-7	Run 1223-3	Run 1227-4	Run 1229-11	Run 1228-8	Run 1228-6	Run 1227-7	Run 1222-1	Run 1229-9
Steam[1/]											
Stripping steam (lb/gal fresh feed)	1.03	1.04	1.01	0.98	1.06	1.04	1.01	1.00	1.07	1.13	1.03
Total steam (lb/gal fresh feed)	1.46	1.45	1.45	1.39	1.48	1.44	1.42	1.41	1.52	1.47	1.48
Caustic											
Stoichiometric dose (%)[2/]	112	91	61	112	91	60	112	91	60	0	0
Addition rate (lb NaOH/gal sour water)	0.0005	0.0004	0.0003	0.0005	0.0004	0.0003	0.0005	0.0004	0.0003	0	0
Feed											
H_2S (ppm)	2968	3070	3148	3072	2952	3132	2898	2999	3034	2611	2653
NH_3-N (ppm)	2066	2400	2500	2100	2400	2400	2133	2433	2466	2450	2366
pH	9.4	9.1	9.6	9.4	9.4	9.1	9.6	9.7	9.2	9.4	9.2
Bottoms											
H_2S (ppm)	9.3	15.2	16.1	8.3	17.4	15.8	15.8	15.1	26.0	16.2	16.7
NH_3-N (ppm)	1	1	13	1	11	12	12	15	14	18	16
pH	7.6	9.4	9.0	8.9	9.1	8.9	9.4	9.5	8.6	7.9	8.8
H_2S remaining (%)[3/]	0.3	0.5	0.6	0.3	0.6	0.5	0.5	0.5	0.9	0.6	0.6
NH_3 remaining (%)	0.0	0.0	0.6	0.0	0.5	0.5	0.5	0.6	0.6	0.8	0.7
Temperatures											
Feed (°F)	153	154	151	154	151	154	154	151	150	162	151
Reflux (°F)	169	166	163	161	170	170	169	164	170	165	166

1/Stripping steam is the amount of steam leaving feed tray. Total steam is the steam fed to the column minus the steam equivalent of column heat losses. Fresh feed includes any water added with the caustic.

2/Ammonia residual is 20 ppm NH_3-N or 1.43 meq/l. 1.43 meq/l is the 100% stoichiometric caustic addition rate.

3/Based on an average feed composition of 2954 ppm H_2S and 2338 ppm NH_3-N.

TABLE E-5. REFINERY F: BENCH SCALE STRIPPING RUNS WITH MULTIPLE CAUSTIC INJECTION POINTS

	Caustic Injection Points		
	Feed-Middle (Run 13-13)	Feed-Middle (Run 13-13)	Feed-Middle (Run 14-14)
Steam*			
Stripping Steam (lb/gal fresh feed)	1.10	1.10	1.10
Total steam (lb/gal fresh feed)	1.57	1.52	1.45
Caustic			
Stoichiometric dose (%)†	112	91	112
Addition rate (lb NaOH/gal fresh feed)	0.0005	0.0004	0.0005
Feed			
H_2S (ppm)	3116	3101	2980
NH_3 (ppm)	2266	2233	2333
pH	9.1	9.1	9.1
Bottoms			
H_2S (ppm)	16.0	16.0	15.3
NH_3 (ppm)	12.0	10.0	14.0
pH	9.2	9.3	9.3
H_2S remaining %‡	0.5	0.5	0.5
NH_3 remaining %	0.5	0.4	0.6
Temperatures			
Feed (°F)	154	154	151
Reflux (°F)	163	163	168

*Stripping steam is the amount of steam leaving the feed tray. Total steam is the steam fed to the column minus the steam equivalent of column heat losses. Fresh feed includes any water added with the caustic.

†Ammonia residual is 20 ppm NH_3-N or 1.43 meq/ℓ is the 100% stoichiometric caustic addition rate.

‡Based on an average feed composition of 2954 ppm H_2S and 2338 ppm NH_3-N.

APPENDIX F

HIGH PRESSURE LIQUID CHROMATOGRAPHY OF REFINERY STRIPPED SOUR WATERS

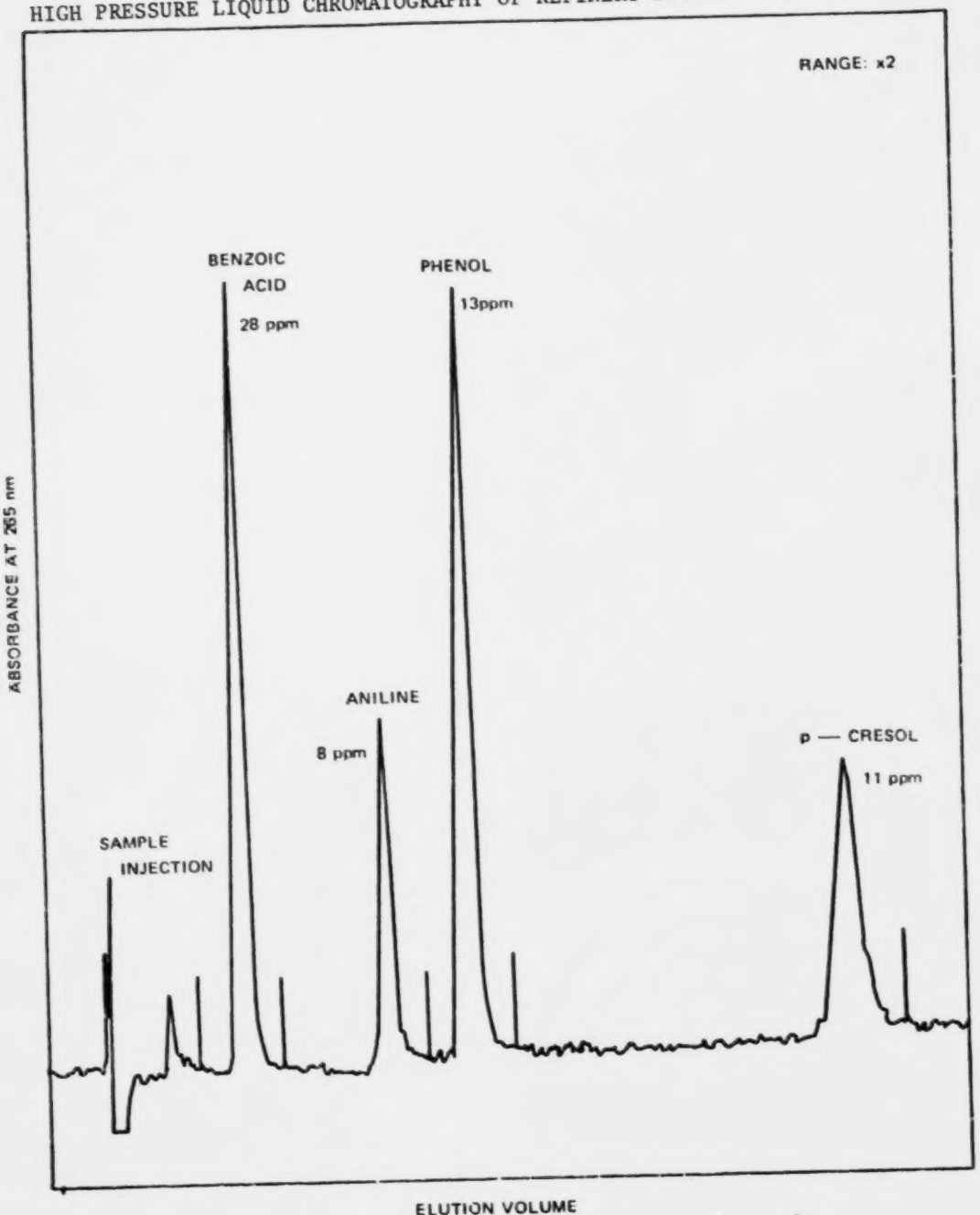

Figure F-1. HPLC analysis of standard compounds.

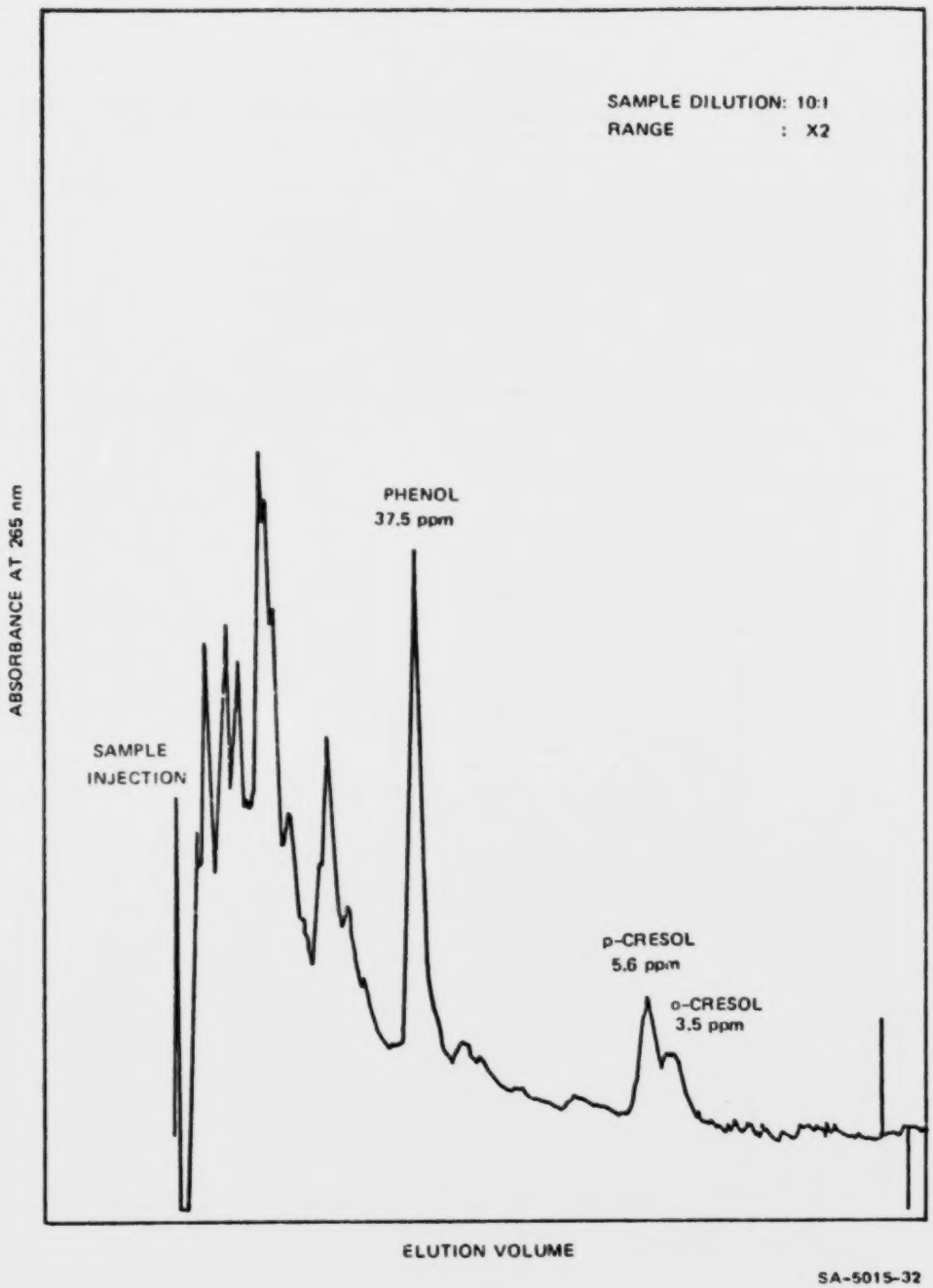

Figure F-2. HPLC analysis of stripped sour water from Refinery A.

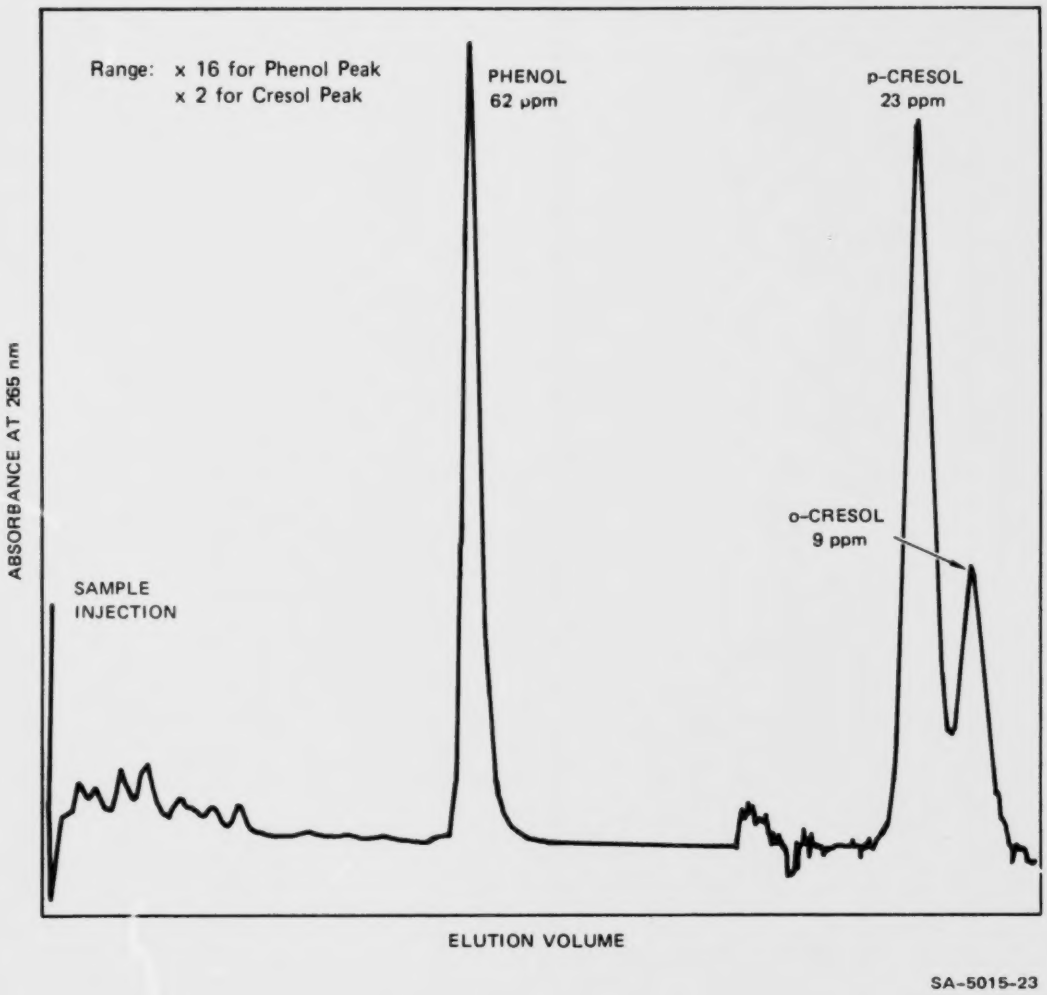

Figure F-3. HPLC analysis of stripped sour water from Refinery C.

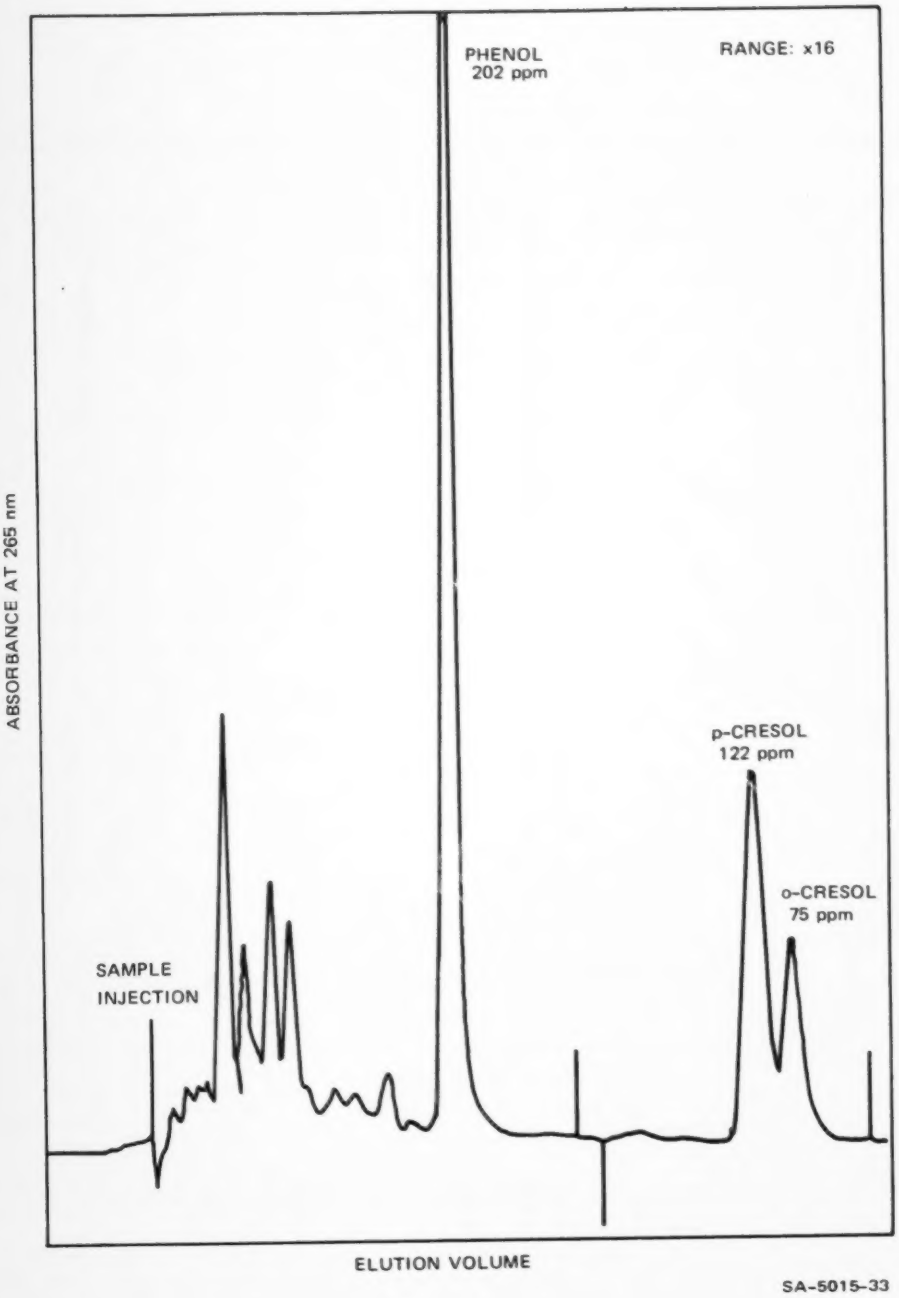

Figure F-4. HPLC analysis of stripped sour water from Refinery D.

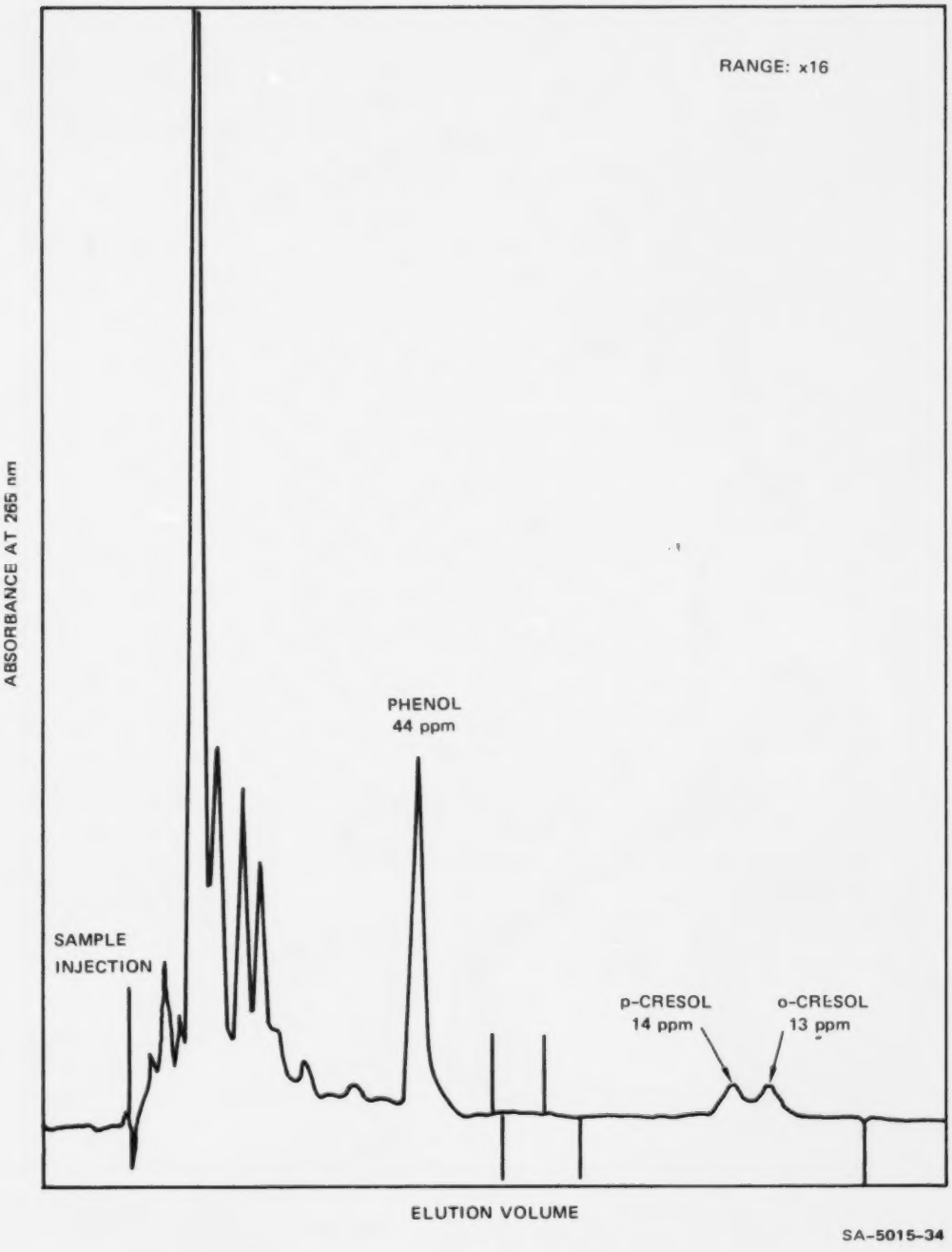

Figure F-5. HPLC analysis of stripped sour water from Refinery E.

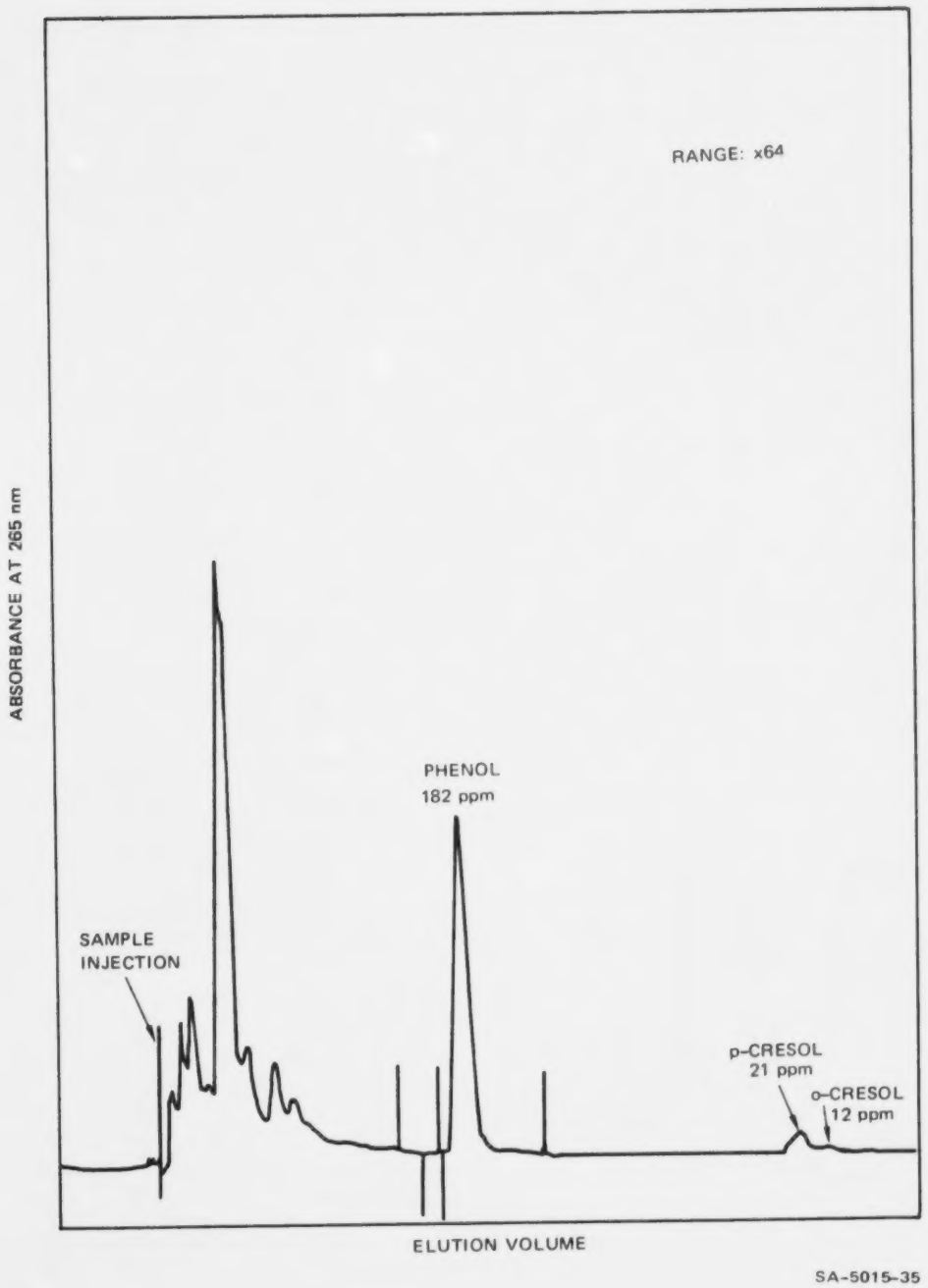

Figure F-6. HPLC analysis of stripped sour water from Refinery F.

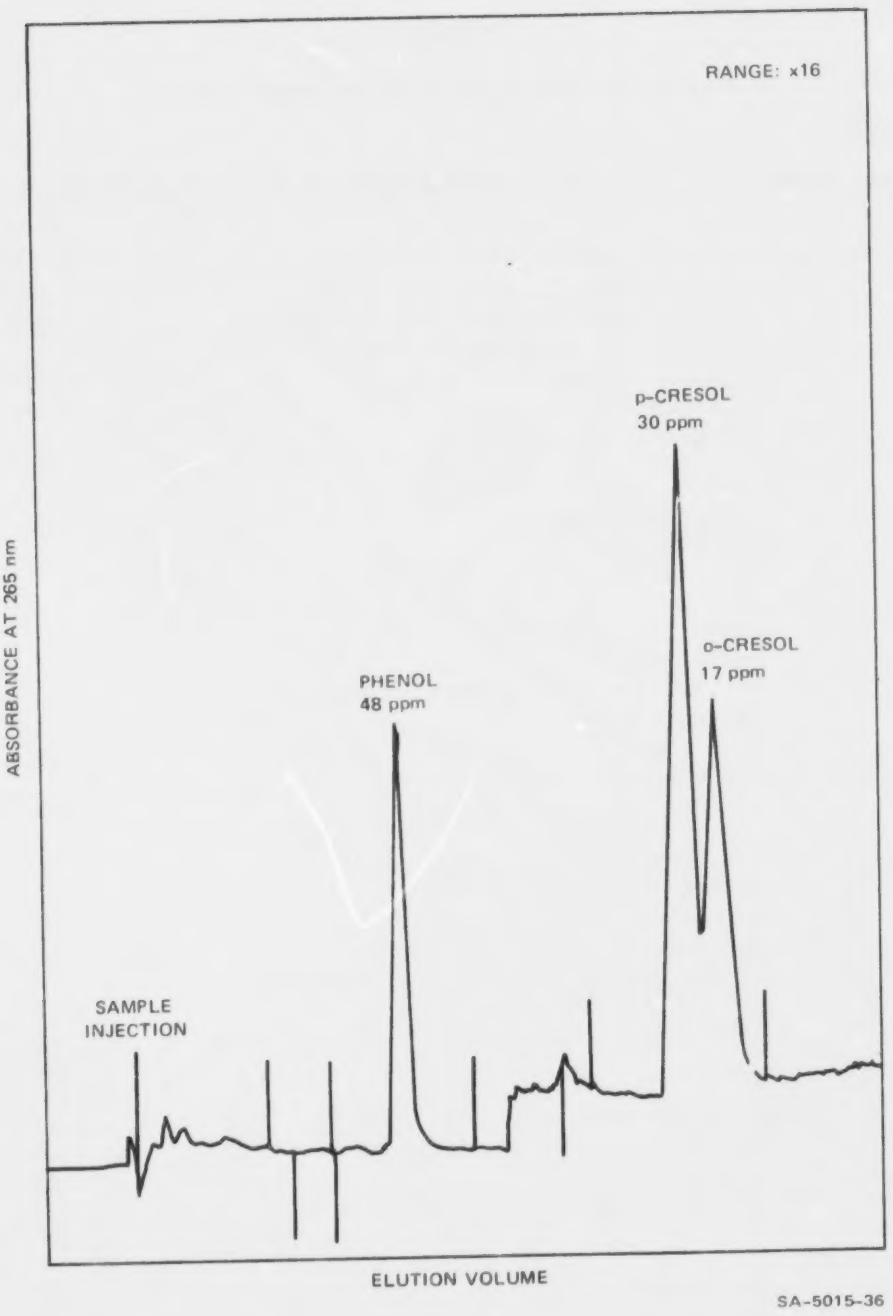

Figure F-7. HPLC analysis of stripped sour water from Refinery G.

APPENDIX G

SOURCES OF SOUR WATERS IN REFINERY SAMPLES

TABLE G-1. SOURCES OF SOUR WATERS IN REFINERY SAMPLES

Refinery	Sour Water Source	Flow (percent)
A	Delayed coker feed fractionation	19
	Delayed coker produce fractionation	26
	Hydrocracker feed vacuum tower	21
	Dehexanizer overhead	<1
	Reformer feed overhead	4
	Non-phenolic waters	30
		100 (58 gpm)
B	Hydro cracking	100
C	Cat cracking	
	Coking	
	Crude distillation	
	Hydrofining	
	Cat cracker feed hydrotreating*	
	Hydrocracking*	
	Slop tanks	
	Flare drums	
		100 (350 gpm)
D	Cat cracking	37
	Coking	22
	Vacuum still	17
	Reforming	8
	Hydrocracking jet fuel hydrotreating	8
	Crude distillation	4
	Alkylation	4
		100 (640 gpm)
E	Crude distillation	17
	Distillate fuel desulfurization	9
	Coking	45
	Cat cracking	29
		100 (890 gpm)
H	Cat cracking	80
	Coking	20
		100 (75 gpm)

*Normally sent to another stripper which was undergoing turn around at the time of sampling of refinery stripped sour water.

APPENDIX H

CONVERSION OF ENGLISH UNITS TO METRIC UNITS

TABLE H-1. CONVERSION OF ENGLISH UNITS TO METRIC UNITS

English Unit	Multiply by	To get Metric Unit
lb	0.4535	kg
gal	3.785	ℓ
lb/gal	119.8	kg/m^3

Temperature Conversion

^oF	^oC
160	71.1
165	73.9
170	76.7
175	79.4
180	82.2
185	85.0
190	87.8
195	90.6
200	93.3
205	96.1
210	98.9
212	100.0

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